

TECHNICAL METHODS OF
ORE ANALYSIS
FOR
CHEMISTS AND COLLEGES

TECHNICAL METHODS OF ORE ANALYSIS

FOR

CHEMISTS AND COLLEGES

BY

ARTHUR J. WEINIG

*Director, Experimental Ore Dressing and Metallurgical Plant
Colorado School of Mines*

AND

WILLIAM P. SCHODER

Owner and General Manager, Heirloom Company, Denver, Colo.

BASED UPON THE TEXT BY
THE LATE ALBERT H. LOW

ELEVENTH EDITION

Sixth Printing

NEW YORK
JOHN WILEY & SONS, Inc.

LONDON: CHAPMAN & HALL, LIMITED

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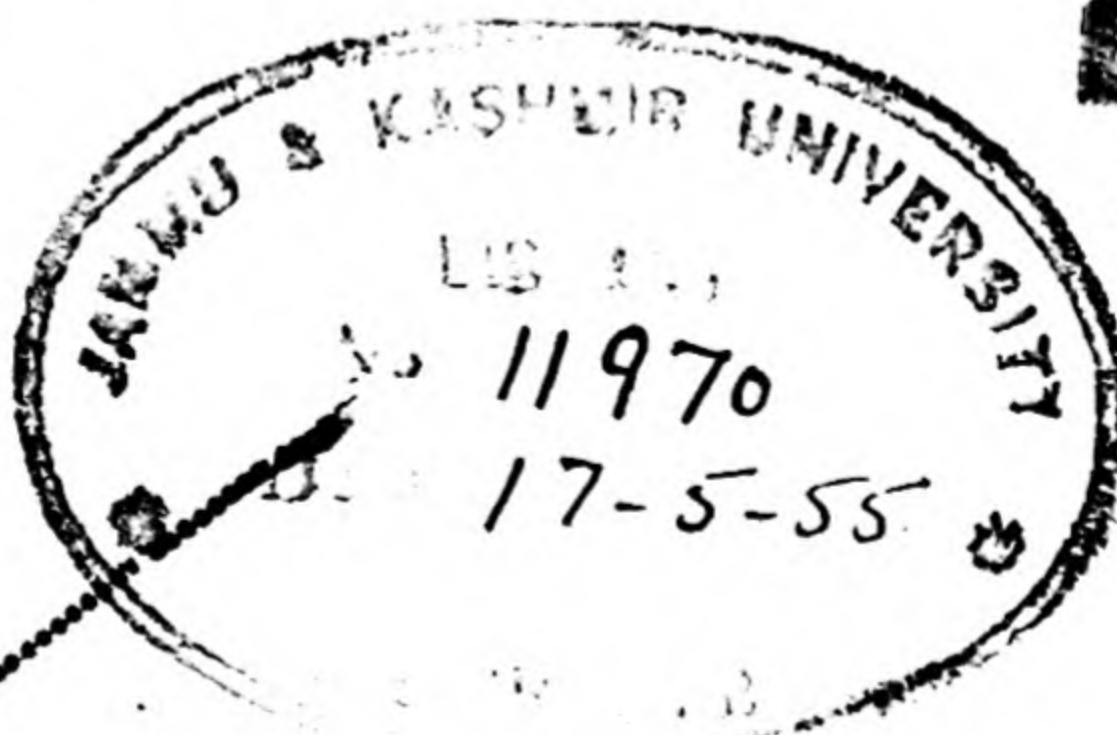
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ELEVENTH EDITION

Sixth Printing, February, 1954



PRINTED IN THE UNITED STATES OF AMERICA



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PREFACE TO THE ELEVENTH EDITION

"Technical Methods of Ore Analysis" by the late Dr. A. H. Low has been a standard reference book in mine, smelter, mill, and student laboratories. The work has been revised in the present edition to bring the quantitative analysis of ores up to date.

This revision retains with corrections all the original material of Dr. Low's work which is still valid. The important changes are (1) the uniform presentation of methods; (2) the introduction of recently established methods; and (3) the use of spot tests as an aid in analytical work.

Information is given regarding the chemical properties of the more common minerals with their chemical factors in order to help the analyst recognize the ore constituents more readily. The gravimetric and volumetric factors have been recalculated in accordance with the 1938 International Atomic Weights.

A bibliography is included for the benefit of those who are interested in additional references on ore analyses and related analytical methods.

This revision is primarily the work of W. P. Schoder. My part has been supervising and making available analytical methods applicable for new ores and processes.

Acknowledgments are included in the subject matter of the book. Special acknowledgments are due the American Chemical Society through Arthur B. Lamb, editor of the *Journal*, for permission to use the 1938 Atomic Weight Table, and Dr. G. E. F. Lundell, Chief of the Chemistry Division, National Bureau of Standards, U. S. Department of Commerce, for permission to reprint analytical procedures for fluorine, magnesium, molybdenum, and phosphate rock.

A. J. WEINIG

Golden, Colorado
January, 1939

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TECHNICAL METHODS OF ORE ANALYSIS

CHAPTER I

SEMI-MICRO METHODS

The development in recent years of qualitative tests for the elements, applicable to minute amounts of ores, through the use of reagents which are more or less specific in their reaction, are of inestimable value to the analytical chemist not only as preliminary qualitative tests and tests for purity of gravimetric precipitates, but also as a source of information for interfering elements during the course of an analysis. The information gained in the analysis of a complex ore often allows the analyst to modify the procedure or make a precautionary separation without loss of the analysis, and offsets any inaccuracy in the final result due to the removal of the minute amount of material necessary for the tests.

The following semi-micro methods or "spot tests" have been selected, from the hundreds of reactions now available in the chemical literature, on a basis of their lack of interference by other elements. It is to be hoped that eventually tests as specific as those of α -benzoinoxime for copper, xanthic acid for molybdenum, and dimethylglyoxime for nickel, may be discovered for all the elements. A great many semi-micro reactions exceedingly applicable under the proper conditions, may be found in the references listed in the bibliography. The organic reagents required in this type of work, though many of them are quite expensive, are used in such small amounts as to render the cost negligible. One gram of reagent, properly handled, will serve for hundreds of determinations.

I. APPARATUS REQUIRED

1. Spot plate of white glazed porcelain
2. Spot plate of black glazed porcelain

A clear glass spot plate which may be used over a background of any color has recently been placed on the market.¹

¹ H. Schäfer, *Mikrochimica Acta*, 1, 144, 1937.

3. Porcelain micro crucibles

These may be obtained in black or white glaze and have a capacity of about 0.5 ml. or 10 to 12 drops.

4. Test tubes. 75 by 100 mm.

In most tests, these tubes are more convenient when cut to a length of 35 to 40 mm.

5. Test-tube holders

The holders shown in Figs. 1 and 2 may be easily constructed from a piece of clock spring or piano wire.



FIG. 1.

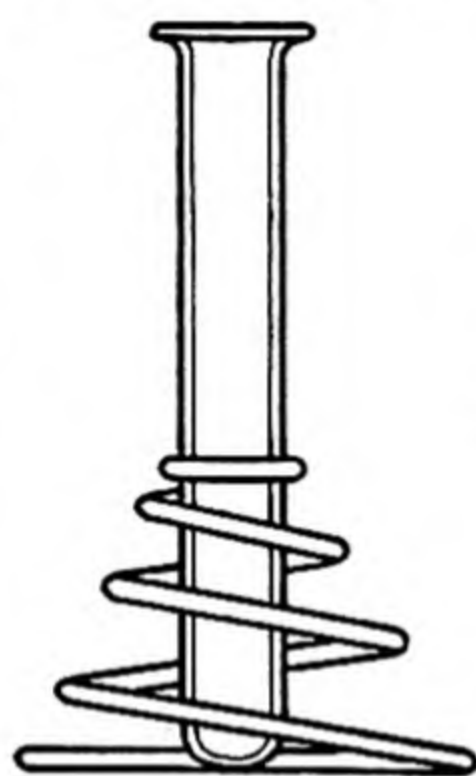


FIG. 2.

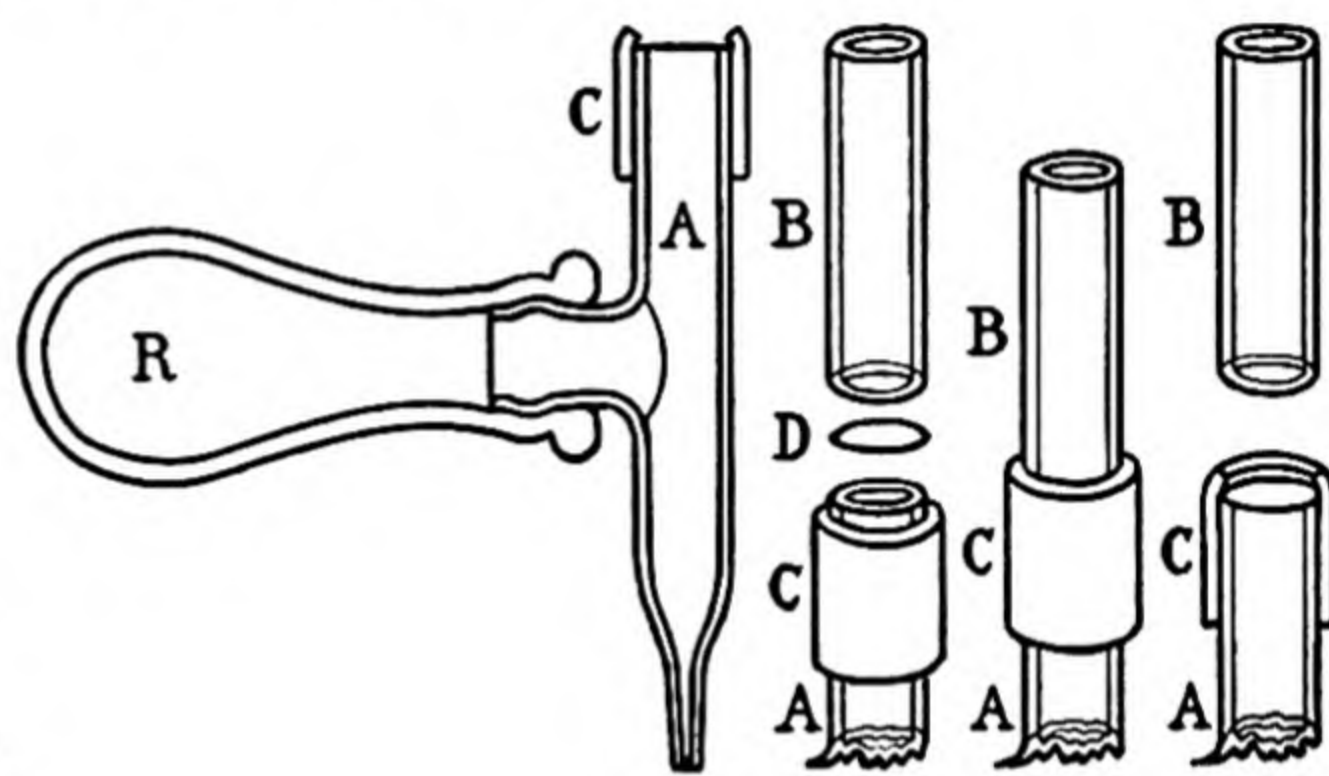


FIG. 3.

6. Filter tubes

The filtering tube pictured in Fig. 3 is a modified form of that described by Caley.² The micro filter papers used with this apparatus are readily made from any grade of filter paper by means of a hand punch such as is used for perforating loose-leaf notebook paper. Medium-walled glass tubing of the same outside diameter as the small papers is formed into a T-tube, one arm being drawn out to form a dropper. The side arm is upset and fitted with a rubber dropper bulb; the top arm, opposite the dropper tip, is ground flat; and a small piece of rubber tubing is slipped over the end. The tube is made ready for filtering by holding the filter paper (D) on the flat ground surface of the arm (A) by means of a piece of glass tubing (B) and sliding the rubber tubing (C) just far enough over the paper to hold it when the tubing (B) is removed.

The filter tube may be used either by placing a drop of the solution on the filter paper or by immersing the tube end into the crucible, test tube, or receptacle containing the solution to be filtered. The

² E. R. Caley, *Ind. Eng. Chem., Anal. Ed.*, 2, 77, 1930.

bulb is squeezed and the dropper point closed with the finger allowing the solution to be drawn through the paper when the bulb is released. The filtered drop is then discharged from the dropper end. The precipitate on the paper is withdrawn for any further treatment by simply sliding the section of rubber tubing (C) down over the arm (A).

7. Drop Reaction Paper

This paper is preferable to ordinary filter paper for most drop reactions because of its ability to absorb the drop rapidly without allowing too much spread. It is obtainable in sheets which may be used directly or cut into strips of the size in which litmus and other indicator papers are purchased, and saturated with the reagent. Plaster tablets used in blowpipe analyses serve very well as a substitute for drop reaction paper. The tablets are prepared by pouring a thin mixture of dental plaster out on a level glass plate and allowing it to set. If the tablets are marked out with a knife just before the plaster hardens they are then easily broken apart after setting.

8. Droppers

These are easily constructed from glass tubing by drawing one end out to a capillary. They may be used either with or without a rubber bulb.

9. Glass Rods

Various styles of rods made from $\frac{1}{8}$ -inch glass rod are shown in Fig. 4. These are used to advantage for spoons, or for stirring, joining drops, separating particles, and breaking lumps.

10. Metal Loops

Metal loops are convenient for all fusions, the flux forming a molten bead within the loop from which it is easily removed. Platinum wire is used for sodium carbonate or pyrosulfate fusions; and silver, nickel, or iron wire serve for fusions with sodium hydroxide or peroxide. The wire should be mounted in a handle of glass tubing, Fig. 5.

11. Micro Gas-Evolution Tube

The apparatus shown in Fig. 6 is adapted to the detection of evolved gases such as arsine in the Gutzeit test for arsenic. Cut a

small test tube in half, and draw the top half out so as to seat in the lower half. The two parts may be ground together after flaring the lower half a little, or held together by a section of rubber tubing. The reaction paper is placed over the open top end.

12. Blowpipe and Charcoal Sticks

13. Alcohol Lamp

This is easily converted to a micro burner by replacing the regular wick and holder by a cork fitted with the tip and wick from a pocket lighter.

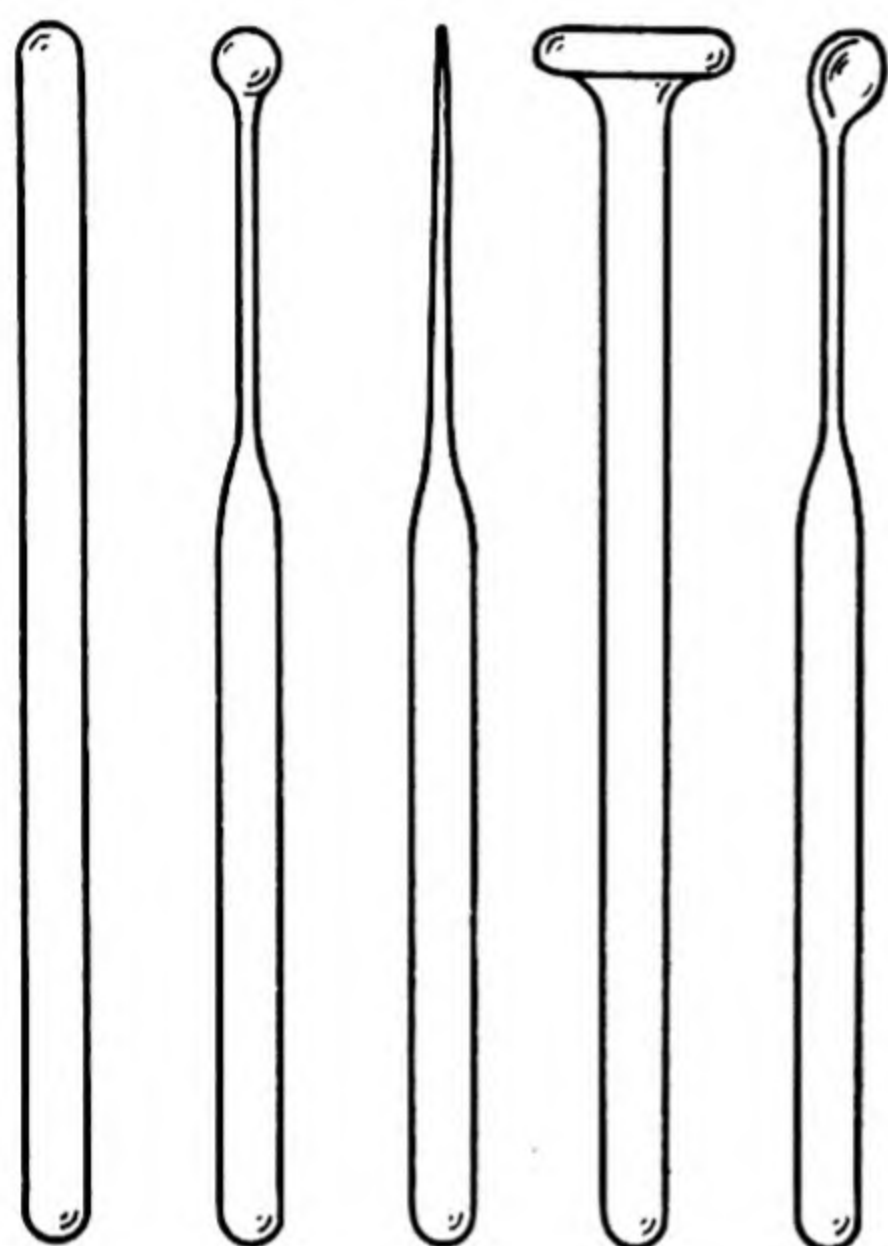


FIG. 4.



FIG. 5.



FIG. 6.

14. Bottles

The three types of bottles shown in Fig. 7 may be obtained from any drug store or laboratory supply house. The iodine dropper bottle (A) in dark glass is especially convenient for dry reagents, the glass rod being flattened on the tip to form a small spoon. The dropper bottle (B) serves well for liquids, and the capsules (C) for holding strips of drop reaction paper impregnated with reagents.

15. Hand Spectroscope

The alkalies and alkaline earths are quickly and easily identified with a hand spectroscope. Low-priced instruments constructed with a small piece of diffraction grating replica may now be obtained.

16. Fluorescence Apparatus

Tests based on the phenomenon of fluorescence are as yet few in number but have an encouraging future. Elaborate equipment for producing ultra-violet light is unnecessary for the tests described

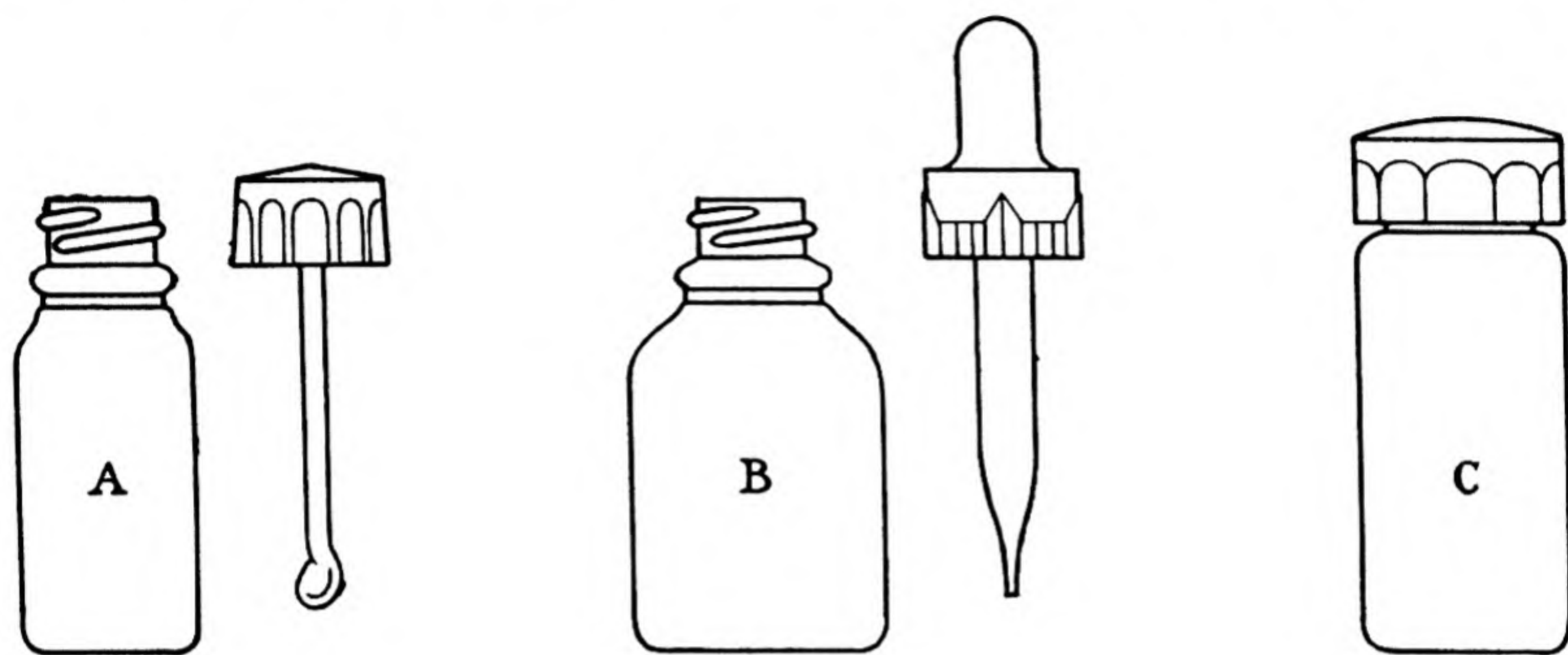


FIG. 7.

here. The apparatus in Fig. 8 can be constructed cheaply from a small 110-volt argon glow lamp, and it provides sufficient ultra-violet light for the purpose at hand.

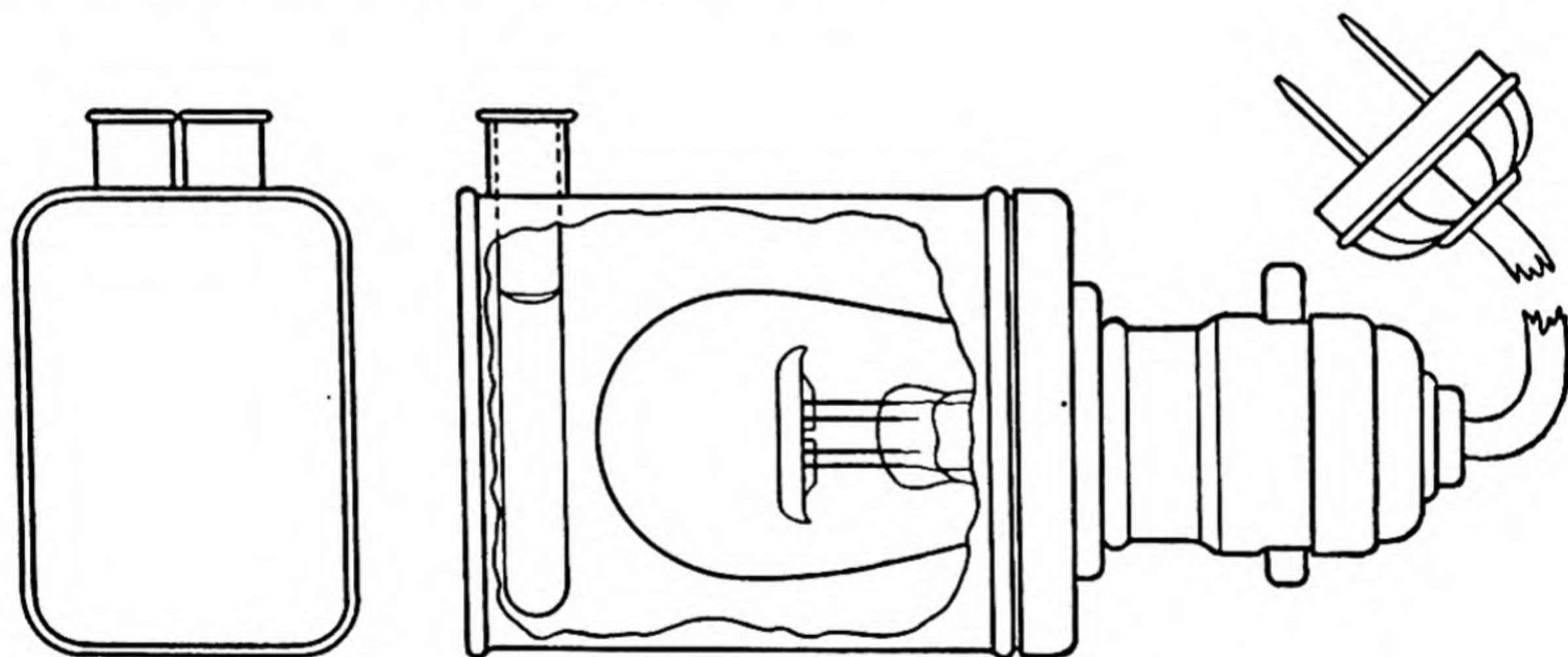


FIG. 8.

II. PRELIMINARY OBSERVATIONS

The analyst frequently does not have the opportunity to examine the material to be analyzed in its original or native form. Hence, any knowledge of the mineral constituents must be obtained from an examination of the finely pulverized sample.

The simplest form of examination is that which has long been used by prospectors, namely, the process of panning. This may be done with a small amount of the material on a large cover glass.

The wet gravity separation of the minerals obtained by this procedure, in conjunction with a small hand lens, will furnish information regarding the mineral constituents of different specific gravity. Sulfides such as pyrite, galena, and sphalerite, are easily identified. Among the heavier minerals other than sulfides which will be the last to be washed from the glass are barite, witherite, cerargyrite, pyromorphite, cerrusite, crocoite, cuprite, hematite, magnetite, wolframite, anglesite, cassiterite, uraninite, vanadinite, and wulfenite. When the mineral is not readily identified by sight, the treatment is of value in that the classified mineral may be separated from the rest of the material and tested by semi-micro methods with a greater freedom from interfering elements. Certain minerals such as molybdenite, graphite, native sulfur, and micas, have a tendency to float on the water and may be skimmed off the surface and tested. Information is also gained regarding the presence of clays, talc, etc., which form slimes.

The addition of dyes or reagents to the water gives stain reactions for certain mineral mixtures. This procedure has received much attention as a quick test for grade in flotation processes but is beyond the scope of this book.

Ignition of the ore preliminary to a test is often of advantage in removing certain elements that interfere, or in converting others to the oxidized state. The elements which volatilize most readily include arsenic, antimony, bismuth, cadmium, lead, mercury, molybdenum, selenium, sulfur, tellurium, thallium, tin, and zinc.

III. SEMI-MICRO PROCEDURES

1. Aluminum

*a. By Pontachrome Blue Black R.*³ Fuse a minute amount of the material in a platinum loop with potassium pyrosulfate. After cooling, crush the melt to a powder and dissolve it in a little water. Add a pellet of sodium hydroxide, filter off a drop or two of the clear solution into a test tube, and acidify with acetic acid. Add 3 drops of a 0.1 per cent aqueous solution of the dye and enough dis-

³ C. E. White and C. S. Lowe, *Ind. Eng. Chem., Anal. Ed.*, 9, 430, 1937.

tilled water to fill the test tube. Place in the fluorescence apparatus with a blank containing the same amount of dye, water, and acetic acid. An orange-red fluorescence denotes the presence of aluminum. The test is applicable to the detection of aluminum in the original material, ammonium hydroxide precipitates, and gravimetric residues such as BeO , $\text{Mg}_2\text{P}_2\text{O}_7$, SiO_2 , and TiO_2 . In tests made from a drop of the unknown solution after treatment with sodium hydroxide and acetic acid, sexavalent chromium and fluorides interfere.

*b. By Tetraoxyflavanol (Morin).*⁴ A saturated aqueous solution of this reagent may be substituted for the Pontachrome dye in the preceding test. A brilliant green fluorescence is produced by aluminum or scandium.⁵

2. Antimony

*a. By Rhodamine B.*⁶ Fuse the sample with potassium hydroxide in a nickel loop, and dissolve the crushed melt in a small amount of water. Filter off a drop of the solution onto the spot plate; add 2 drops of hydrochloric acid, a drop of water, and a pinch of potassium nitrite. On the addition of a few drops of a 0.01 per cent solution of the reagent in 1 : 1 hydrochloric acid, the red color of the dye solution becomes violet in the presence of antimony. **Plate I—1.** Molybdenum and tungsten interfere but may be separated by extraction with alkali carbonates. When applied directly to strong hydrochloric acid solutions, mercury, gold, and thallium also interfere. The method is applicable to the detection of antimony in arsenic distillates, and precipitates such as TiO_2 , BiOCl , SnO_2 , BaSO_4 , and PbSO_4 , after treatment to obtain the precipitate in solution.

b. By Color in the Analytical Procedure. The sulfides of antimony are orange-red in color and confused only with those of cadmium and selenium.

3. Arsenic

*a. By Evolution as Arsine.*⁷ Heat a small amount of the ore with a drop or two of sulfuric acid. Cool, dilute with 2 drops of

⁴ F. Goppelsroeder, *Z. anal. Chem.*, 7, 195, 1868.

⁵ G. Beck, *Mikrochimica Acta*, 2, 9, 1937.

⁶ E. Eegriwe, *Z. anal. Chem.*, 70, 400, 1927.

⁷ Fleitmann, *Ann.*, 77, 126, 1851; Gutzeit, *Pharm. Ztg.*, 24, 263, 1879; Sanger and Black, *J. Soc. Chem. Ind.*, 26, 1115, 1907.

water, and add a small grain of ferrous sulfate to reduce any arsenates present. Add sodium hydroxide till distinctly alkaline, and filter off the solution into the lower half of the evolution apparatus shown in Fig. 6. In the upper half of the apparatus place a small piece of cotton moistened with lead acetate. Add a pinch of aluminum filings to the solution, put the upper tube in place, and set a small piece of filter paper over the top with a drop of saturated solution of mercury bichloride on it. Warm the tube gently. If arsenic is present the paper will be stained yellow to deep brown by the arsine generated. Plate II—1. Stibine does not interfere. The test is applicable to all forms of arsenic compounds. When chlorides or hydrochloric acid are present, solution should be obtained by other means than sulfuric acid and the arsenic must be reduced to the trivalent form before rendering alkaline.

*b. By Stannous Chloride.*⁸ This test is especially adapted to the detection of arsenic in hydrochloric or sulfuric acid solutions. To a drop of the solution on the spot plate add 2 drops of concentrated hydrochloric acid. Place a small grain of stannous chloride on spot paper and then a drop of the strong acid solution on top of it. On warming the paper a brown stain of metallic arsenic will form. Plate II—5. Mercury interferes, giving a black precipitate of metallic mercury. The presence of a minute amount of mercury bichloride, however, tends to hasten the reaction with arsenic.⁹

c. By Color in the Analytical Procedure. The sulfides are bright yellow in color and insoluble in strong hydrochloric acid.

Silver nitrate gives a bright yellow precipitate with arsenites in neutral solution, and a reddish brown precipitate with arsenates.

Arsenates give a yellow precipitate similar to phosphorus and silicon when heated with ammonium molybdate in nitric acid solution.

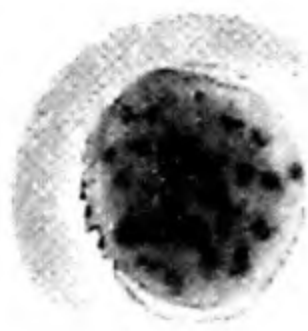
4. Barium

Barium is most easily and definitely detected by use of the hand spectroscope. In the analytical procedure, barium shows up by the insolubility of its sulfate.

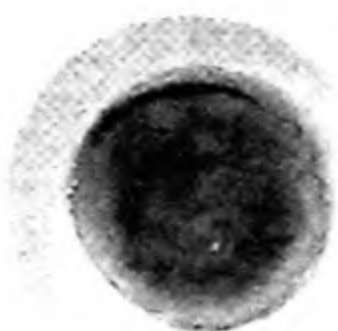
⁸ A. Bettendorf, *Z. anal. Chem.*, 9, 105, 1870.

⁹ W. B. King and F. E. Brown, *Ind. Eng. Chem., Anal. Ed.*, 5, 168, 1933.

PLATE I.



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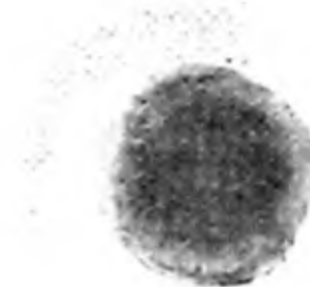
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5. Beryllium

*a. By Quinalizarin.*¹⁰ Fuse a minute amount of the material in a silver, nickel, or iron loop with a pellet of sodium hydroxide.¹¹ When cold dissolve the crushed melt in 3 or 4 drops of cold water, preferably ice water, and filter off 2 drops with the filter tube onto a white spot plate. Place a drop of water in an adjacent impression of the plate, and add 2 drops of quinalizarin solution to both. A blue color imparted to the sample, readily distinguished from the blue-violet color of the blank, denotes the presence of beryllium. **Plate I—2.** The dye solution should be prepared fresh as a 0.05 per cent solution in 0.1 *N* sodium hydroxide.

When the test is performed on a drop of solution, ammonium hydroxide or ammonium salts must be absent if magnesium is present, as the magnesium will not be precipitated with sodium hydroxide and will give a blue color or precipitate identical with that of the beryllium.

6. Bismuth

a. By Bismuth Flux. A small amount of the sample, mixed with bismuth flux (2 parts sulfur, 1 part potassium bisulfate, and 1 part potassium iodide) on a plaster tablet, gives a chocolate-brown sublimate under the oxidizing flame of the blowpipe when bismuth is present. **Plate II—17.**

*b. By Cinchonine and Potassium Iodide.*¹² Dissolve a little of the ore with 2 or 3 drops of aqua regia and evaporate to pastiness. Add a drop of 1 : 1 sulfuric acid, 3 drops of water, and a small crystal of ammonium phosphate. Place a drop of the solution on spot paper which has been saturated with the reagent solution (1 part cinchonine and 2 parts potassium iodide dissolved in 100 parts of 1 per cent nitric acid). A brilliant orange-colored spot denotes the presence of bismuth. **Plate II—6.**

*c. By Sodium Stannite.*¹³ Mix a drop of the solution to be tested on the spot plate with a drop of water, a pellet of sodium hydroxide, and a small pinch of potassium cyanide. Add 2 drops of a freshly

¹⁰ H. Fischer, *Z. anal. Chem.*, 73, 54, 1928.

¹¹ G. Rienäcker, *Z. anal. Chem.*, 88, 29, 1932.

¹² E. Léger, *Z. anal. Chem.*, 28, 374, 1889.

¹³ L. Vanino and F. Treubert, *Ber.*, 31, 1113, 1898.

prepared solution of stannous chloride in sodium hydroxide. A black precipitate indicates bismuth. Plate I—3. Mercury interferes.

7. Boron

*a. By Carmine Red.*¹⁴ Fuse the powdered ore with a pellet of sodium hydroxide in a silver loop. Dissolve the crushed melt in 3 drops of water, and filter off the solution into a micro crucible. Evaporate the solution just to dryness, and add 2 drops of a 0.05 per cent solution of carmine red in concentrated sulfuric acid. In the presence of boric acid the red color turns to blue. Plate I—21. Fluorides and oxidizing agents interfere.

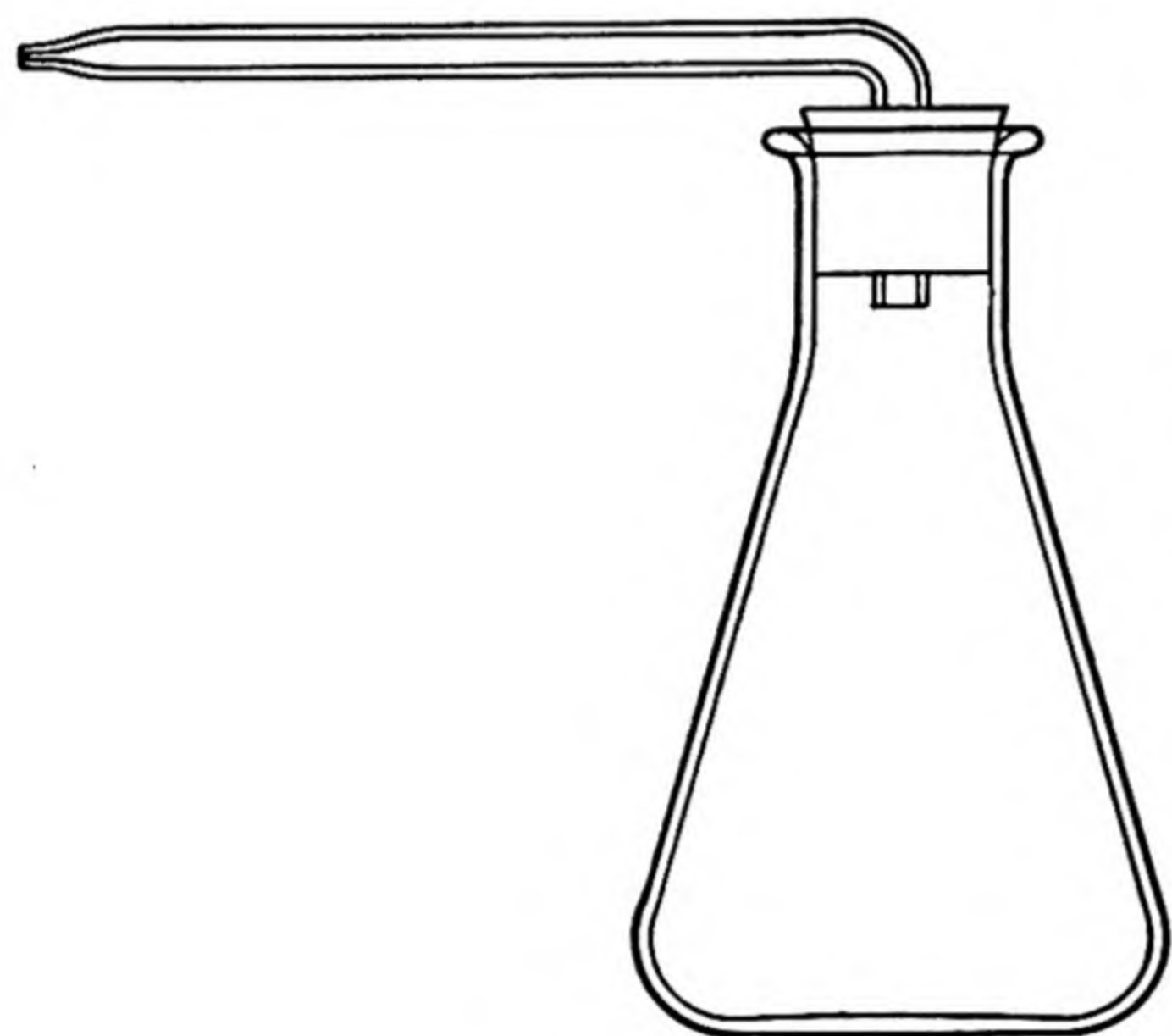


FIG. 9.

b. Flame Test. Boric acid is volatilized as BF_3 or $\text{B}(\text{OCH}_3)_3$ by hydrofluoric acid or methyl alcohol, the volatile compound giving a green-colored flame. Fuse the material as above, and place the crushed melt in a 50-ml. Erlenmeyer flask. Add 5 ml. of methyl alcohol and 2 or 3 drops of hydrochloric acid. Cork the flask with a one-hole stopper containing a bent tube drawn out to a capillary as shown in Fig. 9. Heat the flask

gently while holding the capillary in front of a colorless flame. The alcohol vapor will burn with a green color when boron is present. The test is delicate and specific.

8. Bromine

Bromine is not encountered in ore analysis except when added as an oxidizing agent during the course of an analysis. The excess bromine is then removed by boiling, and it is desirable to know when the last of the bromine has boiled off. Treat a strip of drop reaction paper with starch and potassium iodide (1 part KI and 10

¹⁴ F. P. Zorkin, *J. Applied Chem. (U.S.S.R.)*, 9, 1505, 1936.

PLATE II.



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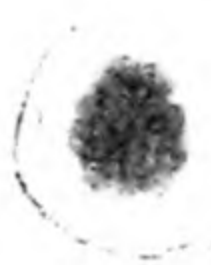
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parts starch dissolved in 200 parts of water), and dry. This paper, held in the vapors being evolved, will be colored blue if bromine is present. **Plate II—19.**

9. Cadmium

a. Sublimate Test. Minerals containing cadmium, when mixed with equal parts of sodium carbonate and powdered charcoal on a plaster tablet, give a greenish yellow to brown sublimate in the oxidizing flame of the blowpipe. **Plate II—18.**

*b. By Diphenylcarbazide.*¹⁵ A great many elements react with this reagent, but under the conditions specified cadmium may be detected in the presence of moderate amounts of the other elements of the H_2S group. A small amount of the precipitate is dissolved in a drop of aqua regia, evaporated to a pasty mass, diluted with a drop of water, and transferred to spot paper that has been impregnated with a saturated alcoholic solution of diphenylcarbazide containing a little potassium thiocyanate and potassium iodide. Upon holding the spot in the vapors of ammonia a blue-violet color is developed in the presence of cadmium. **Plate II—7.**

10. Calcium

Calcium is most definitely detected by the hand spectroscope.

11. Carbon

Carbon compounds are frequently encountered in ore analysis owing to natural carbon content or contamination by flotation reagents and oils. Upon evaporation with sulfuric acid a brown color is obtained which disappears upon repeated treatment with an oxidizing agent such as nitric acid.

12. Chromium

*a. By Diphenylcarbazide.*¹⁶ Mix the ore with equal parts of sodium carbonate and sodium peroxide and fuse in a nickel loop. Dissolve the melt on the spot plate with 2 or 3 drops of 1 : 1 hydrochloric acid and add 2 drops of a saturated solution of the reagent in alcohol. A violet color indicates chromium. **Plate I—4.** Molybdenum and vanadium interfere. The presence of vanadium is de-

¹⁵ F. Feigl and F. Neuber, *Z. anal. Chem.*, **62**, 378, 1923.

¹⁶ P. Cazeneuve, *Compt. rend.*, **131**, 346, 1900; *Chem. Ztg.*, **24**, 684, 1900.

noted by a red color in the acid solution of the melt, and molybdenum may be tested for by xanthic acid.

The method may be applied to a drop of the dissolved ammonia precipitate after oxidation of the chromium to the sexavalent state by potassium chlorate.

b. By Hydrogen Peroxide and Alcohol. Fuse the material as above, and dissolve the melt on the spot plate with nitric acid. Add a drop of amyl alcohol or ether and a drop of 3 per cent hydrogen peroxide. A blue color indicates chromium. Plate I—5.

c. By Color in the Analytical Procedure. Oxidizing alkaline fusions give yellow-colored water-soluble chromates.

Solutions of divalent chromium are blue in color, chromic solutions green or violet, chromites green, chromates yellow, and dichromates orange.

13. Cobalt

a. By Sodium Borate. This test is old, but still extremely useful as the cobalt-blue color of the bead obtained by fusion of the ore (after previous ignition to oxidize) with borax is quite distinctive.

*b. By Potassium Thiocyanate.*¹⁷ Evaporate, to a syrupy condition, a drop of the solution or a small amount of the precipitate or ore to be tested, with 4 or 5 drops of aqua regia. Dilute with 2 drops of water, and add enough of a zinc oxide emulsion to precipitate the iron present. Filter off the solution onto the spot plate. Add a drop of 1 : 1 hydrochloric acid and 6 drops of alcohol; then place a crystal of potassium thiocyanate in the solution. The crystal will turn blue in the presence of cobalt. Plate I—6.

c. By Color in the Analytical Procedure. The dry salts of cobalt turn blue or give a blue solution with concentrated hydrochloric acid, changing to a pink color on dilution.

14. Columbium and Tantalum

*a. By Tannic Acid.*¹⁸ Fuse 2 or 3 mg. of the powdered material in a platinum loop with potassium pyrosulfate. Pulverize the melt, transfer to a small crucible, and heat to boiling with 1 ml. of a 5

¹⁷ W. Skey, *Chem. News*, 16, 201, 1867.

¹⁸ W. R. Schoeller, *Z. anal. Chem.*, 96, 252, 1934; *The Analytical Chemistry of Tantalum and Niobium*, Chapman and Hall, Ltd., 171, 1937.

per cent sulfuric acid solution containing 1 per cent of tannic acid. Filter with the filter tube, inverting the crucible over the tube at the end to obtain the precipitate on the paper. A yellow to orange-red residue indicates tantalum or columbium, the color depending on which element predominates. Plate II—2 and 3.

15. Copper

*a. By α -Benzoinoxime.*¹⁹ Spot paper impregnated with a 2 per cent alcoholic solution of the reagent and dried, when placed in contact with a weak acid solution containing copper and then held over the ammonia bottle, develops a specific green coloration in the presence of copper. Plate II—8. When applying the test to strongly acid or alkaline solutions, the paper may be dipped in ammonia or hydrochloric acid before absorbing the test solution, or the solution may be neutralized on the spot plate.

b. By Color in the Analytical Procedure. Cupric salts are green in acid solutions, turning light blue on reduction to the cuprous state. On addition of ammonia a deep blue solution is obtained when an appreciable amount of copper is present.

With the alkali hydroxides cuprous salts give a yellow precipitate; cupric, a blue precipitate.

The melts from fusions are usually colored blue-green or green by copper.

Potassium ferrocyanide gives a red-brown color or precipitate with weak acid solutions of copper. Plate I—24.

16. Fluorine

*a. By Zirconium and Alizarin.*²⁰ Fuse the material with sodium carbonate and sodium nitrate in a platinum loop. Crush the melt and place on the spot plate. Add 3 or 4 drops of the reagent solution and enough 10 per cent hydrochloric acid to dissolve the melt. When fluorine is present the red color of the zirconium lake is decolorized to a clear yellow solution. Plate I—7. Decolorization should take place within 15 seconds. The reagent solution is prepared by mixing equal volumes of a 0.1 per cent aqueous solution of sodium alizarin sulfonate with a 0.1 per cent solution of zirconium nitrate in 20 per cent hydrochloric acid.

¹⁹ F. Feigl, *Ber.*, 56, 2032, 1923; *Mikrochem.*, 1, 75, 1923.

²⁰ J. H. de Boer, *Chem. Weekb.*, 21, 404, 1924.

The test may be applied directly to flourspar or flourapatite by placing the dry powdered mineral on the spot plate, adding 2 or 3 drops of the reagent solution,²¹ and rubbing the powder with a glass rod.

17. Iron

a. By Complex Cyanides. Iron is easily obtained in slightly acid solution, and the test may then be made on the spot plate, on spot paper, or with indicator papers prepared by saturating with the reagent.

Potassium ferrocyanide gives a blue color (Prussian blue) with ferric salts. Plate I—9. Copper, uranium, molybdenum, cobalt, and nickel, which give color reactions with the reagent, may be separated by ammonium hydroxide or ammonium carbonate.

Potassium ferricyanide gives a blue color (Turnbull's blue) with ferrous salts. Other elements such as silver, bismuth, cobalt, and manganese interfere when present in quantity.

Potassium thiocyanate gives a blood-red color with ferric salts. Plate I—8. Fluorides, phosphates, borates, and organic salts decrease the sensitivity.

*b. By Dimethylglyoxime.*²² To a drop of the acid solution add ammonia till alkaline. Filter with the filter tube, and transfer the precipitate and paper to the spot plate. Add a drop of hydrochloric acid, a small crystal of stannous chloride, and 2 or 3 drops of the reagent solution (1 per cent dimethylglyoxime, and 5 per cent ammonium tartrate, in strong ammonium hydroxide). A brilliant red color denotes the presence of iron. Plate I—10. The test is very sensitive and may be applied directly to hydrochloric acid solutions provided that nickel and appreciable amounts of cobalt and copper are absent.

18. Lead

*a. By Potassium Iodide and Stannous Chloride.*²³ This test is adaptable to all kinds of materials after converting the lead present to lead sulfate. Solid materials such as galena or cerussite may be evaporated with a drop of sulfuric acid, a drop of barium chlor-

²¹ F. Feigl, *Mikrochem.*, 7, 13, 1929.

²² L. Tschugaeff and B. Orelkin, *Z. anorg. Chem.*, 89, 401, 1914.

²³ N. Tananaev, *Z. anorg. Chem.*, 167, 81, 1927.

ide solution added to neutralize the excess acid, and the reagent applied directly to the residue. Solutions are effectively treated by placing a drop of normal sulfuric acid on spot paper, followed by a drop of the test solution, a drop of 10 per cent barium chloride, and a drop of the reagent solution prepared by dissolving a small grain of stannous chloride in a drop of hydrochloric acid and adding 5 drops of a 5 per cent solution of potassium iodide. An orange-colored spot indicates lead. Plate II—9. The test is useful for detecting minute amounts of lead sulfate in gravimetric barium sulfate residues by simply applying the reagent solution.

19. Lithium

The presence of lithium is readily detected by the hand spectroscope.

20. Magnesium

*a. Quinalizarin.*²⁴ Fuse the powdered ore with sodium carbonate in a platinum loop. If sulfides are present the material should be ignited before fusing. Dissolve the crushed melt in 2 drops of 1 : 1 hydrochloric acid and add ammonium carbonate until in excess. Filter off the solution into a micro crucible, evaporate to dryness, and ignite. Add a drop of 10 per cent hydrochloric acid and add a 0.05 per cent solution of the dye reagent in 0.1 *N* sodium hydroxide until alkaline. A blue color or precipitate indicates the presence of magnesium. Plate I—22. All tests for magnesium depend on the absorption of a dye reagent by magnesium hydroxide with or without a color change. Consequently, best results are obtained when the other groups and ammonium salts are absent.

21. Manganese

a. By Oxidation to Permanganic Acid. The unknown material is best ignited at a red heat and a small amount fused with sodium carbonate in a platinum loop. A green-colored melt is usually proof of manganese. The crushed melt is dissolved in 1 : 1 sulfuric acid in a small test tube. In testing hydrochloric acid solutions, a drop may be taken to fumes with a drop of sulfuric acid.

²⁴ F. L. Hahn, H. Wolf and G. Jäger, *Ber.*, 57, 1394, 1924.

The sulfuric acid solution of manganese will give a purple color of permanganic acid when heated with any of the following reagents:

1. A drop of silver nitrate and a few milligrams of ammonium persulfate.²⁵

2. A drop of nitric acid, a drop of phosphoric acid, and a small grain of potassium periodate.²⁶

3. Two drops of nitric acid and a few milligrams of sodium bismuthate.

4. Two drops of nitric acid and a few milligrams of lead peroxide.²⁷

*b. By Oxalic Acid and Sodium Nitrite.*²⁸ This procedure is especially adapted to the detection of manganese in the presence of large amounts of iron such as in an ammonia precipitate. Small amounts in a precipitate of calcium oxalate may be readily detected.

To a minute amount of the precipitate on the spot plate add a drop of a saturated solution of oxalic acid and a pinch of sodium nitrite. A red color indicates manganese. Plate I—11.

c. By Color in the Analytical Procedure. The melts from oxidizing fusions are colored green. Brownish black MnO_2 is precipitated in nitric acid and potassium chlorate digestions, or in alkaline solutions with bromine or hydrogen peroxide.

22. Mercury

*a. By Diphenylcarbazide.*²⁹ Mix the ore with powdered iron, and introduce a small amount of the mixture in a short piece of glass tubing sealed at one end. Tap the mixture down into the closed end and place a small piece of crumpled gold leaf in the open end. Heat the mixture, driving the mercury vapor up to the gold leaf. When cool, break the tube and place the amalgamated gold on the spot plate. Add a drop of nitric acid, 4 or 5 drops of water, and a drop of a saturated solution of the reagent in alcohol. A blue color or precipitate is formed by the mercury. Plate I—12.

²⁵ H. Marshall, *Chem. News*, **83**, 76, 1901.

²⁶ H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, **39**, 2366, 1917.

²⁷ W. Crum, *Ann.*, **55**, 219, 1845.

²⁸ W. Prandtl, *Ber.*, **49**, 1613, 1916.

²⁹ F. Feigl and F. Neuber, *Z. anal. Chem.*, **62**, 370, 1923.

b. By Copper Foil. A clean piece of copper foil placed in a dilute acid solution containing mercury is amalgamated. The gray deposit formed becomes silvery and lustrous when polished with a cloth.

23. Molybdenum

*a. By Xanthic Acid.*³⁰ Fuse a minute portion of the sample with sodium peroxide in a silver loop. Dissolve the crushed melt in a few drops of water, and filter the solution onto the spot plate. Add a small grain of potassium ethyl xanthate (or other xanthate), and acidify with acetic acid. A rose to magenta red color indicates molybdenum. Plate I—13.

The reagent may be used as a test paper for molybdenum in acid solutions by fixing the xanthate reagent in strips of spot paper as the stable cadmium xanthate.³¹ The paper is impregnated with a saturated solution of potassium ethyl xanthate and dried, then immersed quickly in a 10 per cent solution of cadmium acetate, rinsed with water, and dried. Copper, cobalt, nickel, iron, chromium, and uranium interfere under exceptional conditions.

b. By Color in the Analytical Procedure. Digestions with sulfuric acid to fuming, on being allowed to cool and absorb moisture from the air, turn blue.

Weak acid solutions give a brown color with potassium ferrocyanide.

Hydrogen peroxide gives a yellow color with molybdenum in acid solutions, a red-brown color in ammoniacal solutions.

Alkaline sulfides produce yellow, orange, brown, or blue solutions according to the concentration and degree of reduction.

With potassium thiocyanate the reduced compound in acid solution gives a red color similar to that of ferric salts. Plate I—8.

24. Nickel

*a. By Dimethylglyoxime.*³² Nickel ores may be put in solution by digestion with aqua regia. Evaporate off the excess acid, and take up the soluble salts in dilute hydrochloric acid. Place a drop of a 1 per cent solution of dimethylglyoxime in alcohol on the spot

³⁰ S. L. Mallowan, *Z. anorg. Chem.*, 108, 73, 1919.

³¹ B. L. Clarke and H. W. Hermance, *J. Ind. Eng. Chem., Anal. Ed.*, 9, 293, 1937.

³² L. Tschugaeff, *Ber.*, 38, 2520, 1905.

paper. Put a drop of the test solution in the center of the wet spot; follow by another drop of the reagent solution, and finally by a drop of strong ammonium hydroxide. Each drop is allowed time enough to be absorbed before the next is added. In the presence of nickel a pink spot is formed. Plate II—10.

b. By Color in the Analytical Procedure. Acid solutions of nickel are green in color, giving a blue-colored solution upon the addition of ammonia.

The melts from fusions with alkaline carbonates are colored green.

The hydroxide precipitated by the fixed alkalies is green and becomes black on oxidation by bromine.

25. Phosphorus

*a. By Ammonium Molybdate and Benzidine.*³³ Place a small portion of the pulverized ore (or a drop of the acid solution to be tested) on a strip of spot paper, and press flat with a spatula or knife blade. Put a drop of ammonium molybdate reagent solution containing 15 per cent of tartaric acid over the spot of ore and heat gently over the hot plate or a small flame for half a minute. Add a drop of a saturated solution of benzidine in acetic acid and hold the paper over the ammonia bottle. A deep blue color indicates the presence of phosphorus. Plate II—11. When large amounts of phosphorus are present the canary-yellow color of the ammonium phosphomolybdate formed may be detected without the use of the benzidine solution.

26. Potassium

Potassium is best detected by the color of its flame. Small amounts of potassium in the presence of large amounts of sodium are easily seen by viewing the flame through a didymium glass filter. In the presence of other elements which give flame colorations the hand spectroscope should be used.

27. Rare-Earth Elements

The rare-earth group is best detected in the ammonium hydroxide precipitate after removal of the hydrogen sulfide group. Dissolve a small amount of the precipitate on a black spot plate with a

³³ F. Feigl, *Z. anal. Chem.*, 61, 454, 1922; 74, 386, 1928; 77, 299, 1929.

drop of concentrated hydrochloric acid. Add a drop of a saturated solution of ammonium oxalate and 5 drops of water. A white turbidity indicates the presence of the rare-earth group.

Cerium may be detected readily in the presence of the other rare earths and members of the ammonium hydroxide group by arsanilic acid.³⁴

Dissolve the ammonia precipitate in dilute sulfuric acid on the spot plate and add a drop or two of a 0.1 *N* sodium hydroxide solution of the reagent. A pink color indicates cerium. Plate I—14.

28. Selenium

*a. By Sodium Sulfite or SO₂.*³⁵ Heat a few milligrams of the ore in a micro crucible with a drop of nitric acid. Add 3 or 4 drops of a saturated solution of sodium carbonate and boil. Filter with the filter tube, and place the filtered drop on spot paper. Add a drop of a saturated solution of sodium sulfite and a drop of concentrated hydrochloric acid. An orange to red spot indicates selenium. Plate II—12.

29. Silver

*a. By p-Dimethylaminobenzalrhodanine.*³⁶ Silver separates in analytical procedures as the chloride and usually remains with the insoluble material. Treat the silver chloride precipitate or the washed insoluble residue on the filter paper with a drop of the reagent solution followed by a drop of dilute nitric acid. A violet color indicates silver. Plate II—13. The reagent solution is prepared by mixing equal parts of a saturated aqueous solution of potassium cyanide and a saturated alcoholic solution of the reagent. Silver in solution may be detected by placing a drop of the solution on spot paper followed by a drop of 1 : 1 hydrochloric acid, a drop of water, a drop of the reagent solution, and a drop of dilute nitric acid.

30. Sodium

The sodium line of the spectrum offers the simplest means of detection of this element.

³⁴ J. F. Miller, *Ind. Eng. Chem., Anal. Ed.*, **9**, 181, 1937.

³⁵ H. Rose, *Chem. News*, **5**, 185, 1862; E. Keller, *J. Am. Chem. Soc.*, **19**, 771, 1897.

³⁶ F. Feigl, *Z. anal. Chem.*, **74**, 380, 1928.

31. Strontium

Strontium is easily confused with calcium and lithium in the flame test. By means of the hand spectroscope, strontium in a mixture of the three elements is readily detected.

32. Sulfur

a. By the Hepar Reaction. Mix the ore with equal parts of sodium carbonate and powdered charcoal and melt in the reducing flame of the blowpipe on a charcoal stick. Place the cooled melt on a strip of spot paper impregnated with a solution of silver nitrate, and add a drop of water. A brown stain indicates sulfur. Plate II—14.

b. By Lead Acetate. The analyst is often required to remove hydrogen sulfide from solution by boiling. By holding a strip of paper impregnated with lead acetate in the vapor of the boiling solution, the presence or absence of H_2S is easily detected. Plate II—20.

c. By Sodium Nitroprusside. This reagent may be substituted for the lead acetate used above. The strips of spot paper are impregnated with a saturated solution of the reagent and dried. When testing for H_2S in the vapor of a boiling solution they should first be moistened with a drop of ammonia. Plate II—21.

33. Tellurium

a. By Sulfuric Acid and Tin. Place a small pinch of the powdered ore in a porcelain micro crucible. Add 4 or 5 drops of concentrated sulfuric acid and heat to boiling. Remove from the heat and drop in a small piece of tin foil. A bright red color develops immediately around the tin and spreads through the liquid, if tellurium is present. Plate I—23. Selenium gives a bright orange precipitate of free selenium which is dissolved in the acid to produce a green-colored solution, while the more brilliant red color developed by the tellurium remains. Upon dilution of the strong acid solution the red color of the tellurium disappears while the selenium again appears as red metallic selenium.

34. Tin

*a. By Cacotheline.*³⁷ Mix the ore with an equal amount of potassium cyanide and a minute amount of litharge. Place the mixture in a small depression in a charcoal stick and heat in the reducing flame of the blowpipe. Place the cooled melt on an iron plate and crush with a tap of the hammer. Remove the flattened lead bead from the crushed mass and place it on the spot plate. Add a drop of hydrochloric acid, 2 drops of water, and a drop of a saturated aqueous solution of the reagent. A violet color is formed if tin is present. Plate I—15.

35. Titanium

*a. By Chromotropic Acid.*³⁸ Fuse a minute portion of the ore (previously ignited if sulfides are present) with potassium pyrosulfate in a platinum loop. Dissolve the crushed melt on the spot plate in 2 or 3 drops of water, and add a small drop of a hydrochloric acid solution of stannous chloride. Add 2 or 3 drops of a 5 per cent solution of the reagent or place a drop of the solution on paper impregnated with the reagent. A red-brown color indicates titanium. Plate I—16.

*b. By Tannic Acid.*³⁹ Dissolve the crushed bisulfate melt in a small test tube in 1 or 2 ml. of a saturated solution of ammonium oxalate. Add about 100 mg. of ammonium chloride and 20 mg. of tannic acid. Boil gently. An orange-red precipitate indicates titanium or columbium. Plate II—2.

*c. By Hydrogen Peroxide.*⁴⁰ Dissolve the bisulfate melt in dilute sulfuric acid and add a drop or two of 3 per cent hydrogen peroxide. A yellow to orange coloration is formed by titanium. Plate I—17. Molybdenum, cerium, and vanadium interfere.

36. Tungsten

a. By Stannous Chloride. Ignite the material at a low heat to oxidize any sulfides, and fuse the residue with potassium pyrosulfate in a platinum loop. Dissolve the melt with 1 cc. of 1 : 1 hydro-

³⁷ G. Gutzeit, *Helv. Chim. Acta*, 12, 720, 1929.

³⁸ N. A. Tananaev and G. A. Patschenko, *Z. anorg. Chem.*, 150, 163, 1926.

³⁹ W. R. Schoeller and A. R. Powell, *Analyst*, 53, 264, 1928.

⁴⁰ H. Schönn, *Z. anal. Chem.*, 8, 380, 1869.

chloric acid in a small porcelain crucible. Add a small grain of stannous chloride and stir in a little paper pulp. On decanting the liquid and squeezing the pulp between the fingers, the pulp will be tinted a bluish color in the presence of tungsten. Plate II—4. The test may be applied to the insoluble residue from acid digestions for the presence of tungstic acid.

37. Uranium

a. By Potassium Ferrocyanide. Dissolve the material in aqua regia in a small test tube and evaporate just to dryness. Take up the residue in a few drops of dilute hydrochloric acid, add ammonium carbonate in excess, and heat to boiling. Transfer to the spot plate, and filter off the solution with the filter tube. Acidify with hydrochloric acid, and add a drop of the reagent solution. A brown color indicates uranium. Plate I—18. Copper and molybdenum interfere. The reaction may be applied on spot paper. In the presence of iron and copper, the addition of sodium thiosulfate to the solution will reduce the iron and precipitate the copper. On placing a drop on spot paper followed by a drop of the reagent solution, a brown ring of the uranium salt will form around the copper-iron spot. Plate II—16.

b. By Color in the Analytical Procedure. Uranium salts in acid solution are yellow or green.

Alkali hydroxides precipitate the yellow diuranate or the pale green uranous hydroxide.

Fusions with sodium carbonate are colored yellow by appreciable amounts of uranium; fusions with sodium peroxide are colored deep yellow to red.

38. Vanadium

*a. By Dimethylglyoxime.*⁴¹ Digest a small portion of the powdered material in a micro crucible with a drop of aqua regia, and evaporate to dryness. Take up the residue in 4 drops of 1 : 1 hydrochloric acid, evaporate to about one-half the volume, and add a small grain of ferric chloride. Add 2 or 3 drops of a 1 per cent solution of dimethylglyoxime in strong ammonia. A brilliant pink color indicates vanadium. Plate I—10.

⁴¹ F. Ephraim, *Helv. Chim. Acta*, 14, 1266, 1931.

b. By Color in the Analytical Procedure. Fusions with sodium peroxide dissolved in dilute nitric acid give a red color. Plate I—19. The ignited material or minerals such as carnotite, vanadinite, and descloizite give a red color when treated with concentrated hydrochloric acid, the color turning green on dilution.

Vanadium gives a red, yellow, blue, green, or violet coloration in acid solutions according to the degree of reduction.

Ammonium hydroxide solutions when treated with H_2S give a violet color with vanadium.

39. Zinc

*a. By Cobalt-Mercury-Thiocyanate.*⁴² Digest the material with hydrochloric acid, and filter off a drop with the filter tube. Place the drop on the spot plate, and add a drop of a 0.1 per cent solution of cobalt acetate and a drop of the reagent solution (8 grams of mercury bichloride and 9 grams of ammonium thiocyanate per 100 ml. of water). Add enough solid sodium fluoride to decolorize any red ferric thiocyanate, and rub the plate gently with a glass rod. A blue precipitate forms in the presence of zinc. Plate I—20.

40. Zirconium

*a. By p -Dimethylaminoazophenylarsinic Acid.*⁴³ Fuse a small amount of the ore with sodium peroxide in a nickel loop. Dissolve the melt in 5 per cent hydrochloric acid, and place a drop on filter paper which has been impregnated with a 0.1 per cent alcoholic solution of the reagent containing 5 per cent of hydrochloric acid. Dip the filter paper in hot 1 : 4 hydrochloric acid for a minute. A brown spot indicates zirconium. Plate II—15.

41. Test for Elements Detrimental to Platinum

The easily reducible metals and phosphorus are met with frequently in ore analysis and may cause serious damage to platinum ware unless preliminary measures are taken to remove them.

Heat a portion of the ore mixed with sodium carbonate and powdered charcoal (on a charcoal stick) in the reducing flame of the blowpipe. Crush the fused mass on a cover glass and pan with

⁴² P. Krumholz and S. J. Vasquez, *Mikrochem.*, 15, 114, 1934.

⁴³ F. Feigl, P. Krumholz, and E. Rajmann, *Mikrochem.*, 9, 395, 1931.

a little water for any metallic beads. The easily reduced metals will also usually show a sublimate on the charcoal.

Test for phosphates by the semi-micro procedure already described.

42. Sulfur Dioxide

Saturate and dry strips of spot paper with a 2 per cent aqueous solution of soluble starch containing 0.2 of a per cent of potassium iodate. Upon placing a strip of the treated paper in the vapors being evolved from a boiling solution the presence of SO_2 is readily detected by the reduction of the iodate to iodine which reacts with the starch to give a blue color.

ALUMINUM MINERALS

Mineral Name	Chemical Formula	% Al ₂ O ₃	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Bauxite.....	Al ₂ O ₃ ·2H ₂ O	73.9	White to yellowish, reddish or brownish, dull, and earthy odor	2.55	Si, Fe, Ti, Ca	HF and H ₂ SO ₄	KHSO ₄ or Na ₂ CO ₃
Diaspore.....	Al ₂ O ₃ ·H ₂ O	85.1	3.4	Mg, P, S, and Mn	Insol.	Same
Gibbsite.....	Al ₂ O ₃ ·3H ₂ O	65.4	2.35	HCl, H ₂ SO ₄	Same
Clays							
Kaolinite.....	} Hydrous Aluminum Silicates		White to gray or tinted, earthy odor, and slimy when wet	2.0 to 2.6	Same	Hot H ₂ SO ₄	Same
Halloysite.....							
Bentonites.....							
Cryolite.....	Na ₃ AlF ₆	12.8 Al	White or tinted	3.0	Fe, Mn, Si	H ₂ SO ₄	Same
Corundum.....	Al ₂ O ₃	White to grayish	4.0	Fe, Si	Insol.	Same
Andalusite							
Kyanite.....	} Al ₂ O ₃ ·SiO ₂	63.2	White or tinted	3.2	Fe, Mn, Ti, Ca, Mg	Insol.	Same
Sillimanite.....							
Dumortierite.....	8Al ₂ O ₃ ·B ₂ O ₃ ·6SiO ₂ ·H ₂ O	White to bluish	Same	Insol.	Same

Of the minerals containing aluminum, the majority are insoluble in acids. Spinel, topaz, staurolite, some chlorites and micas are imperfectly or completely decomposed by sulfuric acid or bisulfate fusion. The zeolites, leucite, vesuvianite, cancrinite, sodalite, and nephelite are attacked by hydrochloric acid. Felspars, iolite, zoisite, tourmaline, garnets, etc., are best decomposed by alkaline fusion.

CHAPTER II

ALUMINUM

I. INDIRECT METHOD

A. Application

This method is best applied to ores or products such as bauxite, clays, or refractories, which contain an appreciable amount of aluminum and are relatively free from the heavy metals.

B. Interfering Elements

Of the elements precipitated by ammonia, or effecting the precipitation, those most frequently encountered are iron, manganese, titanium, silica, and phosphorus. Less common are chromium, cobalt, beryllium, zirconium, uranium, vanadium, boron, fluorine, and the rare earths, while elements such as gallium, indium, columbium, and tantalum are either of such small amount as to offer little interference or are rarely met with.

A preliminary examination for elements destructive to platinum (Chapter I, No. 41) should be made before attempting a fusion. If harmful components are present in the ore it is best to make an acid digestion first, filter off the insoluble residue, and recombine with the filtrate after fusion as in C. Spot tests should be applied to the material for boron (Chapter I, No. 7), and fluorine (Chapter I, No. 16).

C. Procedure

a. Take 0.5 gram of the finely ground sample and decompose it, according to its nature, either with acids or by fusion in platinum with 5 grams of sodium carbonate. In the latter case, fuse until clear, and pour the melt upon a chilled plate. A convenient arrangement that avoids contamination of the sample is shown in Fig. 10. The cooled melt presents the following color indications; a green color shows the presence of manganese or nickel; a brown color, an

appreciable amount of iron; a yellow color, chromium or uranium; and a blue color, cobalt, manganese, copper, or molybdenum.

b. Place the crucible and cover in an evaporating dish and dissolve the melt adhering to them with a little hot water. Remove the platinum ware and wash with a fine stream of water, using a little dilute hydrochloric acid if necessary. Add the main portion of the fusion to the solution, cover the evaporating dish, and cautiously add enough hydrochloric acid to dissolve the button and leave the solution distinctly acid. The solution is ordinarily yellow in color owing to the presence of iron; if green or blue in color the presence of vanadium, nickel, copper, or chromium is indicated.

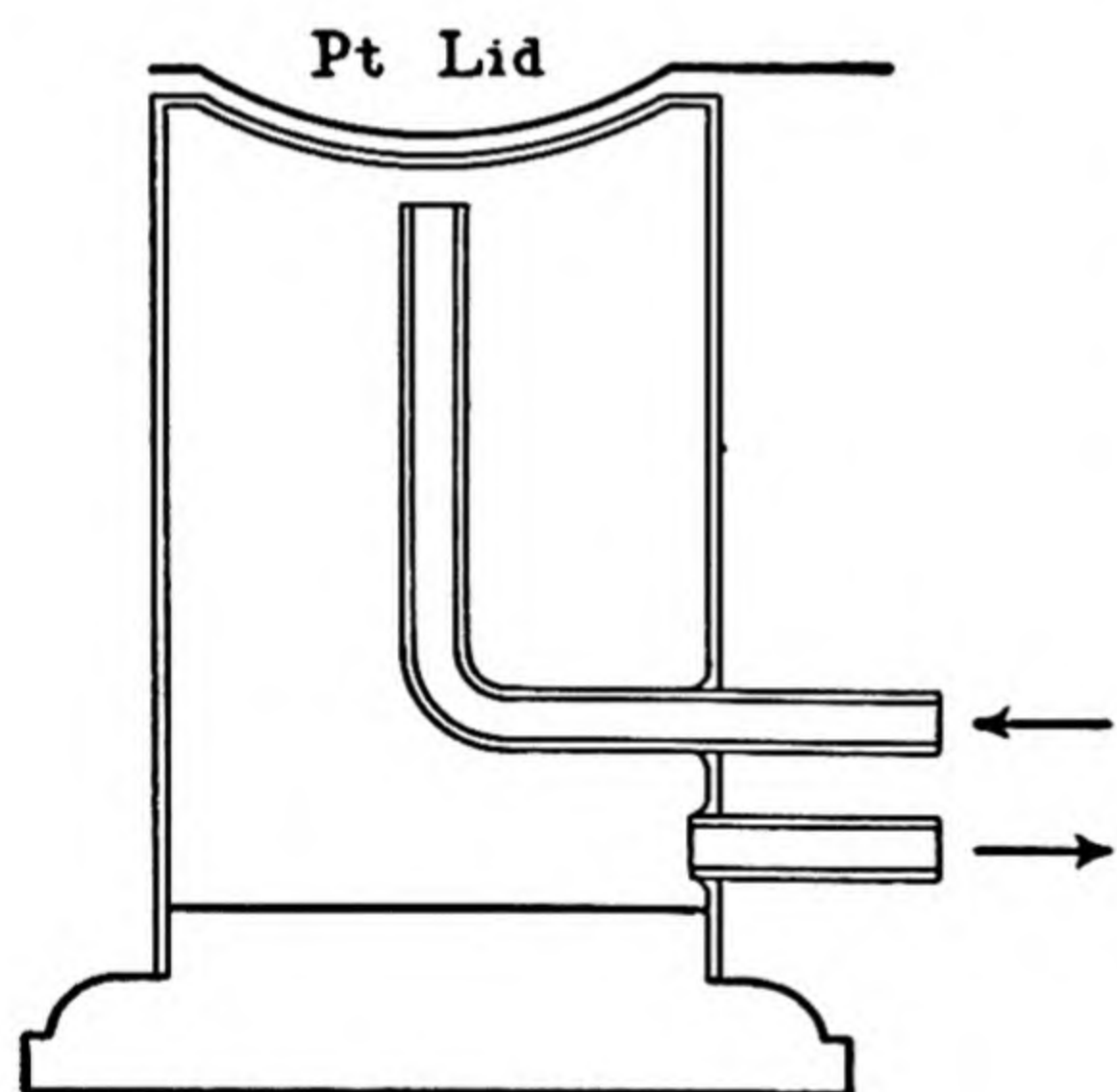


FIG.10.

Evaporate to dryness, and bake the residue to dehydrate the silica. If acids alone have sufficed for the decomposition, the solution may be similarly evaporated.¹

After the evaporation take up in hydrochloric acid, dilute, and filter, washing the residue with hot dilute hydrochloric acid and hot water. Reserve the filtrate. Place the paper and residue in a platinum crucible, and carefully heat until the paper chars and gradually smoulders to an ash.

Do not allow the paper to catch fire, and permit free access to the air. When the carbon is entirely ignited, heat the crucible and contents in the full flame of the burner. Cool, moisten the residue with water, add 4 or 5 drops of sulfuric acid and 5 ml. hydrofluoric acid. Evaporate to fumes on the hot plate, cool and dilute with a little water, and transfer to a small beaker. Add a little bromine water, boil to oxidize the iron present, and combine with the original filtrate, bringing the total volume to about 200 ml.²

¹ Occasionally the use of hydrofluoric acid and a little sulfuric acid in the decomposition of the material, in platinum, may serve to eliminate silica.

² If an insoluble residue is present it may contain aluminum which was not decomposed in the original fusion. It is then necessary to re-fuse this residue before combining with the remainder of the sample.

Place a drop of the solution on a white spot plate and add a drop of hydrogen sulfide water. If no precipitate other than free sulfur is formed, the solution is ready for precipitation by ammonia.

c. Add 2 drops of methyl red indicator solution,³ run in ammonia from a dispensing buret, while stirring until the indicator just changes from red to yellow. Heat to boiling for a minute or two or until the first foamy froth subsides and the bubbles assume a diameter of about $\frac{1}{4}$ inch. If the indicator turns red, add a couple of drops of ammonia and remove from the hot plate. Allow to settle somewhat and filter on a rapid ashless paper, washing well with hot water. If the amount of precipitate is large it is best to redissolve it in hydrochloric acid and repeat the precipitation. It is always safer to do this in any case.⁴

Dry and ignite the mixed hydroxides and weigh as Fe_2O_3 and Al_2O_3 .⁵

d. Fuse the weighed oxides in a silica crucible with a little potassium pyrosulfate, and take up the melt in 100 ml. of 5 per cent sulfuric acid.⁶ Place a drop of the solution on a white spot plate, and add a drop of dilute phosphoric acid and a drop of 3 per cent hydrogen peroxide. A yellow to orange color indicates the presence of titanium, vanadium, or chromium.

Determine the Fe_2O_3 volumetrically, thus arriving at the weight of Al_2O_3 by difference.⁷

³ Hillebrand-Lundell, *Applied Inorganic Analysis*, John Wiley & Sons, Inc., 1929.

⁴ Iron and aluminum, when precipitated in the ordinary way with ammonia, usually carry down with them some of the other constituents in solution, such as calcium, copper, zinc, tungsten, vanadium, and molybdenum. Even though the salts thus carried down are soluble, they cannot subsequently be washed out of the precipitate. When the precipitate is large and the impurities are non-volatile, a considerable error may be introduced. Re-solution of the precipitate, followed by a second precipitation, minimizes this error. Sometimes a third or fourth treatment is desirable. The addition of a little paper pulp before a second precipitation aids in keeping the burnt oxides from caking.

⁵ Alumina, after ignition, is very hygroscopic, and therefore no time should be lost, after cooling in a desiccator, before weighing. The ignited precipitate is likely to gain weight after cooling, even when in a desiccator.

⁶ Silica separating out at this point may be filtered off, burnt, weighed, and deducted from the combined weight of mixed oxides.

⁷ Inspection will sometimes show whether Fe_2O_3 or Al_2O_3 preponderates, the former being reddish brown and the latter white. If the amount of iron present is apparently very small, its determination is best made by varying the usual procedure somewhat. The above residue has been gotten into sulfuric acid solution. Add a small pinch of

D. Modifications for Common Interfering Elements

The solution of the mixed hydroxides, after fusing with potassium pyrosulfate, is nearly neutralized with sodium hydroxide. An equal volume of 10 per cent sodium hydroxide containing a gram or two of sodium peroxide is added slowly while stirring. Heat to boiling and set back on the cooler portion of the plate for about one-half hour. Filter on a strong rapid paper, washing thoroughly with hot water. The precipitate contains the iron and any manganese or titanium present, while aluminum, chromium, vanadium, and phosphorus pass into the filtrate. Reserve the filtrate. Dissolve the precipitate in 100 ml. of 10 per cent sulfuric acid, and divide in equal parts of 50 ml. each.

Ti. To one part add 5 ml. of 3 per cent hydrogen peroxide and 5 ml. of syrupy phosphoric acid. Determine titanium colorimetrically by comparison with a standard titanium solution. See **Chapter XXVII, No. III.**

Mn. To the other 50 ml. add 10 ml. nitric acid, 5 ml. syrupy phosphoric acid, and about 0.25 gram potassium periodate.⁸ Heat to boiling, or until the permanganate color is fully developed. Determine manganese colorimetrically by comparison with a standard solution of potassium permanganate. See **Chapter XVIII, No. V.**

Cr. Determine chromium colorimetrically⁹ in the reserved filtrate by comparison with a standard solution of potassium dichromate. See **Chapter XI, No. III.**

V. Acidify the solution with dilute sulfuric acid, and precipitate the aluminum, vanadium, and phosphorus with ammonia. Filter off the excess alkali salts and wash the precipitate with hot water. Dissolve the hydroxides in dilute nitric acid, dilute, and add a few drops of hydrogen peroxide. Determine vanadium colorimetrically by comparison with a standard solution of ammonium vanadate.

granulated zinc. The mixture soon becomes colorless, showing that all the iron is reduced. Allow the zinc to dissolve completely, then dilute with cold water and filter, receiving the filtrate in a beaker. See that the solution is cold, and titrate at once with standard permanganate solution. Special refinements as to bulk of solution, degree of acidity, and blank test of the zinc are unnecessary. When the amount of iron is apparently large, treat the acid solution just as described in **Chapter XV.**

⁸ Willard and Greathouse, *J. Am. Chem. Soc.*, **39**, 2366, 1917.

⁹ Uranium interferes but is rarely encountered.

P. Boil the solution to remove the excess of hydrogen peroxide. Add a little sulfurous acid to reduce the vanadium, neutralize with ammonia, add 3 ml. nitric acid and 10 grams of ammonium nitrate. Warm the solution, and determine phosphorus gravimetrically with molybdate reagent. See Chapter XXII, No. I, D.

II. DIRECT METHOD

A. Application

The technical determination of aluminum (usually required as Al_2O_3) in ores and metallurgical products is a somewhat troublesome proposition. There seems to be no short and satisfactory method that is applicable to complex substances. The following method though subject to a number of interferences is rapid and adaptable to most ores containing more than 1 or 2 per cent of aluminum.

B. Interfering Elements

Elements which precipitate as phosphates or hydroxides in neutral or slightly acid solutions ($p\text{H}$ 3-6) interfere. Those most frequently encountered are manganese, zinc, and titanium; others such as chromium, vanadium, uranium, beryllium, zirconium, and the rare earths may occasionally be present in sufficient quantity to necessitate preliminary separations.

C. Procedure

a. Treat 0.5 gram of the ore in a platinum dish with 2-3 ml. of strong sulfuric acid and about 20 ml. of strong pure hydrofluoric acid.¹⁰ Evaporate over a water bath or other gentle heat as far as possible, and then cautiously raise the heat until the sulfuric acid is fuming copiously. Allow to cool, add water and a little hydrochloric acid, and warm the mixture until the dish is free from adhering insoluble matter. Now transfer, using as little wash water as possible, to an 8-oz. flask. Add 5 grams of potassium sulfate, 5 ml. of strong sulfuric acid, and one-eighth of a 9-cm. filter. Boil the mixture

¹⁰ Alumina compounds in ores are very likely to consist of silicates not easily decomposed by ordinary acids. The hydrofluoric acid used decomposes these silicates, and the sulfuric acid eventually expels the hydrofluoric acid and converts the bases to sulfates. The material is now in condition for the treatment in a flask that follows. This treatment is given to complete the decomposition and facilitate subsequent operations.

gently at first, to expel water and hydrochloric acid, then, as the sulfuric acid begins to fume, the heat may be increased as strongly as the prevention of undue foaming will permit, finally with the flask in a holder, over a free Bunsen flame, until any free sulfur is entirely expelled and the separated carbon is completely oxidized, leaving a clean mass or melt, with but little free sulfuric acid. The mass is usually white but may have a greenish color due to copper, chromium, uranium, or vanadium. Allow the flask to cool in an inclined position to avoid cracking. The object of the filter paper is to reduce any arsenic or antimony to the *ous* condition, and thus render its subsequent precipitation as sulfide rapid and complete.¹¹

b. After cooling, add 150 ml. of water and 5 ml. of strong hydrochloric acid, and warm the mixture until everything soluble has dissolved. If a trifling residue remains it may usually be neglected. From a larger residue, decant most of the solution through a filter and heat the residue with dilute hydrochloric acid, repeating these operations once or twice if necessary. Calcium sulfate or lead salts may thus be dissolved or greatly reduced in amount.¹² Pour the solutions through the filter, finally transferring any remaining residue, and wash with hot water. Reserve the filtrate. The final residue may consist of a little barium or calcium sulfate or other unimportant substance. Pick up a minute portion of the residue on the loop of a clean platinum wire, touch with a drop of concentrated nitric acid, and hold in the flame of a gas burner. Barium or calcium, if present, may be recognized by the green or red coloration of the flame. See Chapter I.

If its character is thus recognized it may be neglected, but if this is uncertain and aluminum is likely to be present, it is best to treat it further. Ignite filter and contents in a platinum dish until the carbon is consumed. The residue may now either be evapor-

¹¹ If arsenic is left in the *ic* condition, its precipitation by hydrogen sulfide is very slow, as the hydrogen sulfide has to reduce it first to the *ous* condition.

¹² The heating with sulfuric acid and potassium sulfate converts any iron present into anhydrous ferric sulfate. This is usually the most troublesome of the eventually soluble salts to get into solution, as it first has to become hydrated. Even by heating in the presence of hydrochloric acid the solution is frequently very slow. Undissolved anhydrous ferric sulfate, when much is present, usually appears as minute pearly scales by slowly rotating the liquid. When allowed to settle it is not as white as the sulfates of barium, calcium, or lead. Any remaining undissolved is likely to retain aluminum sulfate and thus render the result low.

ated again with a little hydrofluoric and sulfuric acid nearly to dryness, or, if silica is apparently absent, it may be fused with a little mixed sodium and potassium carbonates.¹³ In either case the solution of the product, acidified with hydrochloric acid, may be added directly to the reserved filtrate, without regarding any residue of barium sulfate.

c. The liquid is now an acid solution of the various bases. It should not be too acid, and it is therefore safer to nearly neutralize with ammonia and then reacidify with an excess of 5 ml. of hydrochloric acid.¹⁴ Now dilute to about 300 ml. with hot water, and pass in hydrogen sulfide to precipitate the metals of that group. Ten minutes will usually suffice for this precipitation since any arsenic or antimony is in the *ous* condition and will come down quickly. It is well, however, to have the liquid fairly cool at the end, to insure the complete precipitation of any lead. Filter, washing with water containing hydrogen sulfide and a little acetic acid. Boil the filtrate until all hydrogen sulfide is expelled, and then oxidize the iron to the ferric condition by the cautious addition of 10 ml. of bromine water to the boiling solution.¹⁵ Now dilute to about 400 ml. with cold water and allow to cool to room temperature. Make tests for zinc (Chapter I, No. 39), and titanium (Chapter I, No. 35). The liquid is now ready for the precipitation of the aluminum as phosphate, according to Peter's modification of Wöhler's method,¹⁶ as follows:

d. Add ammonia until the solution becomes brown or dark red in color, according to the amount of iron present, but still contains no precipitate. When there is little or no iron, simply neutralize to faint acidity, using litmus paper. Now add 3.3 ml. of hydrochloric

¹³ The mixed salts are used simply because they fuse at a lower temperature than the single salts.

¹⁴ If the solution is very acid, hydrogen sulfide may fail to precipitate completely all the metals of the group.

¹⁵ Hydrogen sulfide reduces any iron present to the ferrous condition. Bromine water is added to oxidize the iron back to the ferric state. If the hydrogen sulfide were not previously boiled off it would be decomposed by the bromine water and produce an unnecessary precipitation of sulfur. Having the iron in the ferric state permits the proper neutralization with ammonia without causing any of the iron to precipitate. When the cold ferric solution is gradually neutralized with ammonia a soluble brown basic ferric chloride is eventually formed, the neutralization being carried on to the extreme that will not cause a precipitation.

¹⁶ Blair, Chemical Analysis of Iron, 3d ed., p. 250.

acid of 1.2 sp. gr. and 2 grams of sodium phosphate dissolved in water and filtered if necessary.¹⁷ Stir until any precipitate formed is dissolved and the solution becomes perfectly clear again. If the solution should become more and more turbid, cautiously add more hydrochloric acid until it clears. Note the extra amount used, and increase the sodium thiosulfate at the rate of 10 grams for each 3 ml. of acid required. Now add 10 grams of sodium thiosulfate, dissolved in water (and filtered if necessary), and 5 ml. of 80 per cent acetic acid, or 4 ml. of the 99 per cent acid. Heat to boiling, boil thirty minutes, and filter as rapidly as possible on an ashless filter.¹⁸ Wash thoroughly with hot water. If the amount of the precipitate is small it may at once be dried, ignited in a porcelain crucible, together with the filter, and weighed as AlPO_4 . Multiply this weight by 0.4178 to obtain the weight of the Al_2O_3 .

If the precipitate is large in amount it should be redissolved and reprecipitated. Rinse it into a beaker, add a little hydrochloric acid to dissolve it, and then pour through the filter, to dissolve what was not rinsed off, and wash the filter thoroughly. Dilute the filtrate somewhat, if necessary, add ammonia in slight excess, and then re-acidify with acetic acid in slight excess. Heat to boiling, filter, and wash with hot water. Then dry, ignite, and weigh as above described. It is always well to boil again the filtrate from the first precipitate of aluminum phosphate for some time and filter off the precipitate formed on a separate filter. Ignite this in a separate cruci-

¹⁷ The hydrochloric acid added prevents the precipitation of ferric phosphate by the sodium phosphate. When the thiosulfate is added, it completes the neutralization of the mineral acids and sets free sulfurous acid in their place, at the same time reducing the iron to the ferrous condition. Ferrous phosphate is soluble under these conditions and therefore does not precipitate. Acetic acid is added to maintain the presence of a weak acid during the subsequent boiling and thus prevent the precipitation of all other phosphates except aluminum phosphate.

¹⁸ Aluminum phosphate is more or less soluble in cold dilute acetic acid and therefore does not precipitate at once. In the same mixture, heated to boiling, however, it is quite insoluble and comes down together with sulfur that separates from the continually decomposing thiosulfate. Sulfur always precipitates even in the absence of aluminum. It is white at first and therefore indistinguishable from the white aluminum phosphate, but agglomerates and turns yellowish on prolonged boiling. Its admixture with the aluminum phosphate is advantageous, as it facilitates filtration and washing. The filtration is made without delay, while the liquid is boiling hot, on account of the possibility of some of the aluminum phosphate dissolving if the solution is allowed to cool. Even when the precipitation of the aluminum has been complete, the filtrate always becomes turbid owing to the continued precipitation of sulfur.

ble (not weighed), and, if any AlPO_4 is found, brush it in with the main portion. A precipitate of sulfur will thus always be obtained, and the presence of aluminum phosphate can be determined only by igniting it. It is best to repeat this boiling and filtering until the ignited precipitate leaves no residue.

D. Modifications

Large amounts of titanium may be separated by precipitation with sodium hydroxide preceding part C, d of the procedure. Zinc is best removed by precipitation with hydrogen sulfide in dilute sulfuric acid solution.¹⁹

Manganese is only partially precipitated in this method. The final precipitate of aluminum phosphate should be dissolved in 10 ml. of sulfuric acid. Then dilute to 50 ml., add 15 ml. of nitric acid and 0.25 gram potassium periodate, and bring to a boil. Cool, dilute to 100 ml., and compare the color with a standard potassium permanganate solution. See **Chapter XVIII, No. V.**

¹⁹ Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 331.

ANTIMONY MINERALS

Mineral Name	Chemical Formula	% Sb	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Stibnite.....	Sb_2S_3	71.7	Lead-gray, metallic luster	4.5	Pb, Cu, Zn, Hg, As, Fe, Ba, Ca, Ag, Au	HCl, H_2SO_4	
Cervantite.....	$Sb_2O_3 \cdot Sb_2O_5$	78.9	White to yellowish white	4.0	Same	HCl	KOH
Valentinite.....	Sb_2O_3	83.3	White to yellowish white	5.8	Same	HCl	KOH
Senarmontite.....							
Native antimony.....	Sb	Tin-white, metallic luster	6.7	As, Ag, Fe	H_2SO_4 HCl + Br_2	

Antimony minerals are in general soluble in hydrochloric acid, when oxidized or in combination with lead or iron as in jamesonite, boulangerite, berthierite, kermesite, plagionite, etc.

Those containing antimony combined with silver, copper, nickel, cobalt, and mercury, such as pyrrargyrite, tetrahedrite, polybasite, andorite, aramayoite, breithauptite, ullmanite, and livingstonite are decomposed by nitric acid with separation of Sb_2O_5 .

Owing to the volatile properties of antimony in hydrochloric acid solutions and the insolubility of basic salts formed with nitric acid, these acids are not generally desirable for decompositions when antimony is to be determined. Sulfide minerals are best brought in solution by hot sulfuric acid and alkali sulfate, and oxidized minerals by fusion with alkali hydroxide.

The antimony minerals combined with sulfur are practically all gray to black when pulverized except a few such as pyrrargyrite, livingstonite, miargyrite, kermesite, breithauptite, and tetrahedrite, which have a reddish or reddish brown color.

CHAPTER III

ANTIMONY

I. PERMANGANATE METHOD

A. Application

The method may be used on sulfides and most mixed ores containing at least 1 or 2 per cent of antimony. Oxidized ores rich in antimony may fail of complete decomposition by the acid treatment described below, but may be readily decomposed by the procedure set forth in D, b.

B. Interfering Elements

The most troublesome interfering element is arsenic. If arsenic is known to be absent or negligible in amount, the procedure may be shortened by omitting the operations for its removal. Tin is without influence on the antimony result but may prove an annoyance, if much is present, owing to its troublesome sulfide.

C. Procedure

a. Weigh 0.5 gram of the finely ground ore into an 8-oz. flask (a Pyrex flask is best); add 2 grams of anhydrous sodium sulfate, 5–6 ml. of strong sulfuric acid, and one-eighth of a 9-cm. filter paper. The object of the last is to provide organic matter for the reduction of arsenic and antimony to the *ous* condition, thus facilitating the solution of the antimony and also rendering the subsequent precipitation of both metals as sulfides rapid and complete. Heat the mixture, cautiously at first, over a small free flame, then, with the flask in a holder, over the full flame of a Bunsen burner. Continue until any free sulfur is expelled, the separated carbon completely oxidized, and the free sulfuric acid almost entirely driven off. If apparently necessary, add a little more sulfuric acid and run down again.

Allow the mass to cool with the flask on its side, as otherwise the solidifying cake may crack it, or rotate the flask slowly with the holder until the mass solidifies on the sides.

If the mass is green while hot and white on cooling, copper is present. A green color when the mass is either hot or cold indicates uranium and nickel; a brown color when hot and a green color when cold indicate chromium; a blue color when hot and a pink color on cooling indicate cobalt; an orange color before cooling and a yellow color after cooling indicate vanadium. If the cold mass turns a deep blue on the edges after standing, molybdenum is present.

b. When cold, add 25 ml. of hot water and warm gently, without boiling, to disintegrate the cake completely. The insoluble residue, if white, may contain lead, aluminum, silica, barium, or tungsten. If green in color, basic nickel or chromium salts are present. The solution is colored blue by copper, green by nickel, blue-green by vanadium, yellow by uranium, and pink by cobalt or excessive amounts of manganese. Boiling would materially alter the volume of the water and change its relation to the hydrochloric acid next added. Remove from the heat, add 50 ml. of strong hydrochloric acid,¹ and agitate gently, without further heating, to dissolve soluble salts, especially anhydrous ferric sulfate. The mixture is now 2 volumes of strong acid to 1 of water.² Additional heating is avoided at this stage, as it might easily occasion loss of arsenic by volatilization, if arsenic is to be determined, and might also change the relative proportions of acid and water, upon which the separation of arsenic depends.

Test a small drop of the solution for arsenic as directed in Chapter I, No. 3 b.

Pass in a rapid current of hydrogen sulfide for about ten minutes. As any arsenic present is in the *ous* condition, this should be sufficient time for its complete precipitation. A little arsenious chloride in the vapors might escape from the flask. To prevent this possible slight loss it is best to use the arrangement shown in Fig. 11. The thistle tube contains a little glass wool moistened with 5 per cent sodium hydroxide solution. Any arsenic escaping is

¹ In a hydrochloric acid mixture of this strength, antimony will not be precipitated by hydrogen sulfide, while arsenic in the *ous* condition will quickly come down as As_2S_3 .

² Anhydrous ferric sulfate, produced by the effect of concentrated sulfuric acid and heat on iron salts, is most troublesome to dissolve. If much is present it appears as minute pearly scales when the liquid is slightly agitated or rotated. In a warm acid solution it will gradually become hydrated and dissolve.

thus caught and subsequently recovered. Some copper may be precipitated, but no antimony or tin. During the precipitation make a mixture of 25 ml. of water and 50 ml. of strong hydrochloric acid, to be used in the washing. If a bell jar and glass plate are available, so as to permit filtration into a beaker, they may be used with suction, but a filter flask is undesirable, as it necessitates subsequent transference of the filtrate into a beaker.

Filter off the As_2S_3 precipitate, receiving the filtrate in a 600-ml. beaker. Adhering sulfide in the flask or on the delivery tube will be recovered later, but it must be well washed with the acid mixture to remove antimony.

Wash the delivery tube, held over the flask, with the prepared acid mixture, and set it aside temporarily. Now wash out the flask with the same mixture, pouring from the flask over the precipitate, and allowing the filter to drain completely between washings. The antimony is now in the filtrate. If arsenic is to be determined, proceed with the precipitate, flask and delivery tube as directed in **Arsenic, II, C, a.**

Continue with the antimony as follows:

c. Mark the height of the filtrate on the beaker and then dilute with hot water to about $3\frac{1}{2}$ times this height. Pass in a rapid current of hydrogen sulfide for at least ten minutes. The previous delivery tube and flask, if not reserved for arsenic, may be cleansed with ammonia and used for antimony. Filter the precipitated Sb_2S_3 , as before, into a large beaker. The filtrate should be perfectly clear—otherwise refilter. Using hydrogen sulfide water slightly acidified with acetic acid, wash out the beaker and delivery tube and then wash the precipitate six or seven times. This is to remove most of the hydrochloric acid. Reject the filtrate. Wipe out any adhering sulfide in the beaker with a bit of filter paper and place on the precipitate. Reserve the delivery tube.

Place the clean original flask, or a similar one, under the funnel.

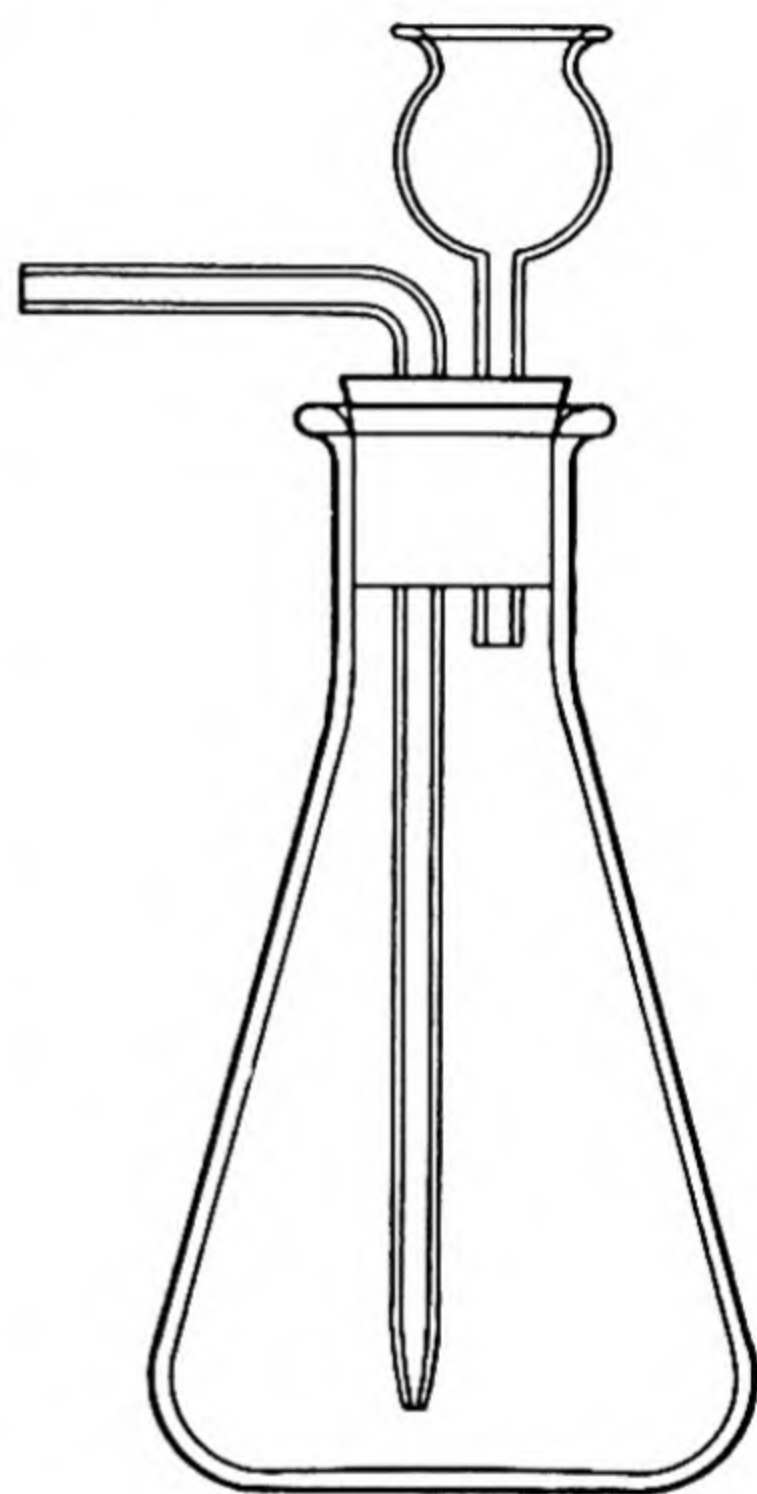


FIG. 11.

Warm about 15 ml. of a 5 per cent solution of sodium hydroxide in a small beaker. Cleanse the delivery tube, held over the funnel, with a few drops of this, and then continue to pour the solution very slowly over the precipitate to dissolve it. Use as little as possible—perhaps 10 ml. Dilute the remainder (or take a little more if necessary) with about 50 ml. of hot water, for washing. Wash the filter six or seven times with this, keeping the bulk of the filtrate as small as possible.

Add to the solution in the flask about 2 grams of anhydrous sodium sulfate and 6-7 ml. of strong sulfuric acid. Support the flask over a small free flame and boil down to small bulk; then, with the flask in a holder, run down, over a strong free flame, as in the original decomposition of the ore, using the same precautions in the cooling. The piece of filter paper for reduction purposes is here omitted as unnecessary.³

d. To the cool residue in the flask add 10 ml. sulfuric acid, 50 ml. of hot water, and 10 ml. of hydrochloric acid. Heat to effect solution, and then boil a short time to expel any possible SO_2 . Test with fuchsine or potassium iodate-starch paper as described in Chapter I, No. 42. Now add 10 ml. more hydrochloric acid and cool completely under the tap. Dilute to about 150 ml. with cold water, and titrate with standard potassium permanganate solution to the usual pink tinge. Antimony is oxidized from the trivalent to the quinquevalent condition. The end point is sharp, but soon fades, owing to the action of the hydrochloric acid present on the permanganate.

The standard permanganate solution used for the iron titration (see Chapter XXXIII) will serve for antimony. The iron value of the permanganate multiplied by 1.0902 will give the antimony value. Or multiply the sodium oxalate value by 0.9086.

D. Modification

a. In the presence of large amounts of tin, dissolve 10 grams of oxalic acid crystals in the filtrate containing the antimony (C, c) previous to diluting and passing in hydrogen sulfide gas.⁴ The tin will be kept in solution and occasion no further trouble.

³ The free sulfur which is always present is a sufficient reducing agent, and, moreover, the antimony is already in a reduced condition at the outset.

⁴ F. W. Clarke, *Chem. News*, 21, 124, 1870.

If arsenic and other elements such as vanadium, thallium, and large amounts of copper, iron, or chromium are absent from the original material, the solution may be titrated with permanganate immediately after decomposition, omitting the precipitations with hydrogen sulfide outlined in C, b, and c.

b. *Decomposition of Oxidized Material.* In a thin spun-iron crucible of about 60-ml. capacity melt about 8 grams of sodium hydroxide (2-3 inches of the stick hydroxide, broken into short pieces). Heat until the moisture is expelled and quiet fusion attained, and then allow to cool. It is a good plan to add a very small pinch of potassium nitrate to the melt just previous to cooling to guard against any subsequent reduction of metal from the ore.⁵

Weigh 0.5 gram of the powdered ore, transfer it to the prepared crucible, cover with a very loosely fitting porcelain cover, and fuse the mixture. Heat very cautiously at first until violent bubbling has ceased, and then with the full flame of a Bunsen burner until quiet fusion is attained. Remove the cover, and pour the melt upon a clean iron plate, or other cold smooth surface. Invert an evaporating dish over the hot cake, to prevent loss if the cake cracks violently apart in cooling.

Set the crucible in a 400-ml. beaker containing 50 ml. of cold water. Cover the beaker and tip the crucible over with a glass rod, so as to admit the water, and add 40 ml. of strong hydrochloric acid. Warm the mixture and turn the crucible about with the glass rod until it appears clean. Remove and rinse the beaker cover, lift the crucible on the rod, and wash off the outside so as to permit handling with the fingers. Now rinse out the inside of the crucible. If any undissolved melt remains, dissolve it with a little hydrochloric acid and rinse into the beaker. Add the cooled melt and porcelain cover, and again cover the beaker. Warm until the cake has dissolved. Lift out the crucible cover with forceps, or by means of a bent iron wire passed through the loop, and wash it.

As a rule the decomposition is perfect and everything goes into solution in the hydrochloric acid, even the silicic acid, except, per-

⁵ The sodium hydroxide contains an excess of water, which it does not give up until melted and heated to dull redness. Unless this water were removed before adding the ore, there would be a large loss from spattering. Sodium peroxide does not have this defect, but, on the other hand, its high oxidizing power often prevents or hinders complete decomposition of the ore.

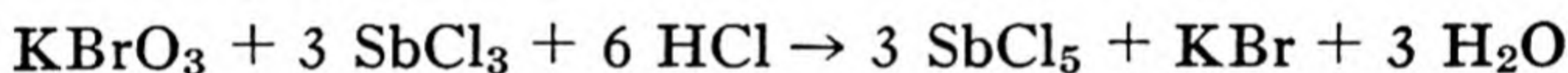
haps, scales of iron oxide from the crucible, to which no attention need be paid. Barium might separate as sulfate, but this is easily distinguishable from undecomposed ore. Now add 2-3 grams of tartaric acid,⁶ and, when it has dissolved, dilute sufficiently and filter if necessary. If gelatinous silica clogs the filter, a few drops of hydrofluoric acid will usually clear it.

A hydrochloric acid solution containing all the antimony, together with sufficient tartaric acid, having been obtained, dilute to about 300 ml. with hot water. Precipitate the antimony with hydrogen sulfide, and then follow the direction given in C, c up to the point where the cold residue is obtained in the flask after the sulfate fusion. From this point, proceed exactly as after the fusion of the ore by the previous method.

II. BROMATE METHOD

A. Application

The following method is based on the reaction



A method based on this reaction was first suggested by Györy and modified by Nissensen, Siedler, and Rowell⁷ for testing hard leads. The present method is a modification of the latter, and is best used on material containing little arsenic, iron, or copper, and not less than $\frac{1}{2}$ to 1 per cent of antimony. It is especially adaptable to the determination of antimony in hard leads and alloys.

B. Interfering Elements

The most probable source of error is the incomplete removal of arsenic or sulfur dioxide.

Oxidation need not be feared if the cover is kept on. The liquid must not be allowed to evaporate to dryness, as antimonious chloride begins to volatilize at about 195° C., and boils at 220° C.

Lead, zinc, tin, silver, chromium, and sulfuric acid have no effect upon the test, but large quantities of calcium and ammonium salts tend to make the result high.

Iron tends to make the results high, but not in as great a ratio as

⁶ This is to prevent the precipitation of a basic salt of antimony when the solution is subsequently largely diluted.

⁷ S. Györy, *Z. anal. Chem.*, **32**, 415, 1893; and H. W. Rowell, *J. Soc. Chem. Ind.*, **25**, 1181, 1906.

copper. Iron is very slightly reduced by sulfurous acid in a strong hydrochloric acid solution, and if, before the sodium sulfite is added to a test, it is boiled down to as small volume as possible and made up again with cold, strong hydrochloric acid, the effect of iron is almost destroyed. With this precaution, 1 per cent of iron raises the test about 0.02 per cent, while 5 per cent has very little more effect. Vanadium must be removed prior to the titration with potassium bromate.

C. Procedure

a. One gram of the finely divided ore or alloy, containing not more than 0.15 gram of antimony, is weighed into a 400-ml. beaker. These quantities may be varied, provided that more of the substance can be conveniently dissolved, and that the amount of standard bromate solution required is within the compass of the buret used. To the sample, 25 ml. of concentrated hydrochloric acid and 5 ml. of the saturated solution of bromine in hydrochloric acid are added; the covered beaker is then placed on a warm iron plate, so that the temperature is not high enough to drive off the bromine before complete solution is effected, and occasionally shaken until complete solution takes place.

Antimony oxides, and precipitates of mixed oxides of antimony and tin which do not dissolve readily in this way, may be fused with eight times their weight of caustic soda in a silver crucible at a dull-red heat, till the mass turns yellowish green.⁸ The fused mass is dissolved in as little water as possible and transferred to a 400-ml. beaker; the solution is acidified with hydrochloric acid and evaporated down to 10 ml., when 20 ml. of hydrochloric acid is added. Copper or vanadium present will impart a green color to the solution.

b. To reduce the antimony, 3 or 4 grams of fresh sodium sulfite crystals is added, the cover and sides of the beaker lightly rinsed down with water, and the liquid evaporated, with the cover on, to 10 ml. or a little less if possible. Although there seems to be little risk of the antimony oxidizing during the evaporation, the cover is better kept on, as it retards the evaporation very little and often saves a test when it, or one near it, spurts through evaporat-

⁸ To avoid loss by spattering, observe the precautions described in I, D, b.

ing too far.⁹ If more than 2 or 3 per cent of arsenic is present, 20 ml. of strong hydrochloric acid and 5 ml. of saturated sulfurous acid are added, and the liquid boiled down again. Test a small drop of the solution for arsenic as given in Chapter I, No. 3 b.

c. To the concentrated solution, 20 ml. of strong hydrochloric acid and 40 ml. of hot water are added, the cover and sides of the beaker are rinsed, and the whole is boiled for one minute to remove traces of sulfurous acid. The standard solution of potassium bromate is now run in, to within a few milliliters of the necessary amount, with constant and thorough stirring, at the rate of not more than 30 ml. every fifty seconds.¹⁰

If lead chloride begins to crystallize, the solution must be boiled again, but otherwise 2 drops of methyl orange solution are added, and the bromate run in drop by drop, till the color of the indicator is destroyed. The solution should be kept at a minimum temperature of 60° C., and should be thoroughly stirred during the titration so that a local excess of bromate never forms, otherwise some of its value is lost before it attacks the antimony. The result is calculated from the equation:

$$\frac{(\text{ml. of bromate required by 1-gram sample} - \text{blank})}{\text{ml. of bromate required by 50 ml. of arsenic solution}} \times 10 = \text{per cent Sb}$$

A blank test should be made occasionally in exactly the same way as above, the sample being omitted, and the result (which should not exceed 0.2 ml.) subtracted from each test.

d. *The Effect of Copper.* Copper is partially reduced by sulfurous acid in a strong hydrochloric acid solution, and, under the conditions of the method given, raises the test in a fairly constant ratio as shown by the following figures:

	GRAM Sb
0.001 gram of copper as cupric chloride in a blank test	= 0.0001
0.005 gram of copper as cupric chloride in a blank test	= 0.0005
0.010 gram of copper as cupric chloride in a blank test	= 0.0012

The quickest and most satisfactory way of obviating the effect

⁹ Sodium sulfite is better than sulfurous acid for effecting the reduction, as it raises the boiling point considerably toward the finish and insures complete volatilization of the arsenic.

¹⁰ A preliminary run on approximately half of the solution, to which methyl orange has been added at the outset, will indicate the approximate end point. This titrated portion may then be added to the rest and the titration completed carefully.

of copper is to dissolve the substance in 15 ml. of nitric acid (1 : 2), evaporate just to dryness, and boil for a few minutes with 50 ml. of 1 per cent nitric acid; allow to settle, and pour off the liquid through a fine filter. Add 30 ml. of 5 per cent solution of ammonium nitrate, boil again, and transfer all the precipitate to the filter, wash two or three times with a hot 5 per cent solution of ammonium nitrate, and dry the filter and precipitate. Separate the precipitate from the filter, and fuse it and the filter ash together as directed above.

Perhaps as exact a way, when the copper amounts to about 1 per cent, is to subtract 0.012 per cent of antimony for every 0.1 per cent of copper, the copper being estimated as follows:

Weigh 0.1 gram of pure copper, dissolve it in nitric acid, and dilute the solution to 100 ml. One milliliter = 0.1 per cent copper, on the basis of 1 gram = 100 per cent.

Add an excess of ammonia to the titrated solution, so as to develop any blue color to be produced by copper. Mix, and allow any precipitate to settle.

Place some water in a similar beaker, run in a definite amount of the copper solution from a buret, make alkaline with ammonia, and dilute the solution to the same bulk as that in the first beaker. By a succession of trials, match the color of the first beaker as closely as possible. Note the amount of copper solution required, and calculate the percentage.

The above simple procedure is not expected to give a very exact result, but is probably quite sufficient for the purpose intended.

D. Solutions Required

a. *Standard Arsenious Chloride Solution.* Into a 500-ml. graduated flask, 0.8123 gram of pure powdered arsenious oxide, dried carefully at 100° C., is weighed. About 5 ml. of 10 per cent sodium hydroxide solution is added, and the flask is shaken and gently warmed until the arsenic is completely dissolved; 5 ml. of strong hydrochloric acid is added, and the solution is made up to the mark with water. Fifty milliliters of this solution, equivalent to 0.10 gram of antimony, is measured off with a pipet, the delivery of which has been checked against the 500-ml. flask. A solution made in this way and kept in a well-stoppered bottle remains unchanged for a fortnight without oxidation.

b. *The Indicator.* One-tenth of a gram of pure methyl orange is dissolved in 100 ml. of hot water. Drops of this indicator should be taken out with a tube to avoid the stain left about the neck of the bottle, as this or an old solution is likely to leave a stain and spoil the sharp finish. Methyl blue and other methyl colors stable in hydrochloric acid generally stain the solution, while indigo turns green toward the finish, and the end is not so easily distinguished as with methyl orange. More of a solution of indigo is also required to produce a sufficient color.

c. *The Standard Potassium Bromate Solution* is approximately 0.05 *N*, and is made by dissolving 1.41 grams of the "pure" salt in 1 liter of water. The theoretical quantity is 1.3918 grams per liter, but the "pure" salt always contains bromide which, however, makes no difference to the test. To standardize the solution, 20 ml. of strong hydrochloric acid is added to 50 ml. of the standard arsenic solution, and the mixture brought just to a boil. Thirty milliliters of the bromate solution is then added, and the titration finished in exactly the same way as in the method below, all the precautions being observed. The solution should be standardized every week, as it loses its strength rapidly.

A 0.2 *N* solution may be used for titrating larger quantities of antimony.

d. *Bromine Solution.* Thirty-five milliliters of pure bromine, thoroughly shaken up with 250 ml. of strong hydrochloric acid, makes a saturated solution, and leaves excess of bromine. The required quantity is conveniently measured by dipping in a pipet without any stem below the bulb and so allowing it to fill.

ARSENIC MINERALS

Mineral Name	Chemical Formula	% As	Descriptive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Arsenopyrite....	FeAsS	46.0	Grayish black	6.0	Pb, Cu, Zn, Sb, Sn, Ba, Ag, Au, Ni, Co, Tl	HNO ₃ + Br ₂ + H ₂ SO ₄ Na ₂ SO ₄ + H ₂ SO ₄	Na ₂ CO ₃ + KNO ₃ Na ₂ CO ₃ + ZnO
Enargite.....	3Cu ₂ S·As ₂ S ₅	19.1	Sooty black	4.4	Same	Same	Same
Native arsenic..	As	Tin-white to gray	5.7	Sb, Fe, Bi, Au, Ag	HNO ₃ , H ₂ SO ₄	

All arsenic minerals, if finely pulverized, may be decomposed by the treatments indicated above. Hydrochloric acid should be avoided owing to the volatility of arsenious chloride.

When finely powdered, most of the sulfide or arsenide minerals such as smaltite, chloanthite, lollingite, and cobaltite are gray to black. A few are brightly colored, such as realgar, orpiment, and proustite, which are orange, yellow, and scarlet respectively. The arsenates, mimetite, scorodite, and pharmacolite, are white; erythrite shows the pinkish to bluish colors of cobalt salts; annabergite the green of nickel salts; and olivenite, euchroite, and chalcophyllite have the green color characteristic of cupric compounds.

CHAPTER IV

ARSENIC

I. DISTILLATION METHOD

A. Application

This method may be applied to all classes of ores or metallurgical products requiring the separation or determination of arsenic. Materials containing 1 per cent or more of arsenic are best determined volumetrically; smaller amounts may be weighed as the sulfide.

B. Interfering Elements

If the distillation is properly performed, none of the common elements offer any serious interference.

C. Procedure

a. Treat 0.5 gram of the ore in a 500-ml. flask as described for antimony under Antimony, I, C, a, and b. Cool the melt, add 25 ml. of hot water, and warm gently, without boiling, to disintegrate the cake completely. Add 15 ml. hydrochloric acid, and digest at a low temperature to dissolve the soluble salts.¹

b. Set up the flask as shown in Fig. 12. Add 5 ml. of hypophosphorus acid and 100 ml. of hydrochloric acid, and make sure that all connections are tight. Adjust the heating unit so that the temperature at no time rises above 108° C. Distil until the volume of the solution in the flask is reduced to about 25 or 30 ml. Remove the stopper, and test a small drop of the solution for arsenic by the method given in Chapter I, No. 3 b. If arsenic is still present add 5 ml. more of hypophosphorus acid and 50 ml. of hydro-

¹ If much silica is present, the solution is likely to bump during the distillation. Filter through a 7-cm. paper into another 500-ml. flask, keeping the volume of the filtrate as small as possible.

chloric acid. Replace the stopper and continue the distillation until the hydrochloric acid added has passed over to the distillate. The process must be continued until all the arsenic has been distilled. If preferred, the last portions of the distillate may be caught in a separate beaker and tested for arsenic by means of hydrogen sulfide.

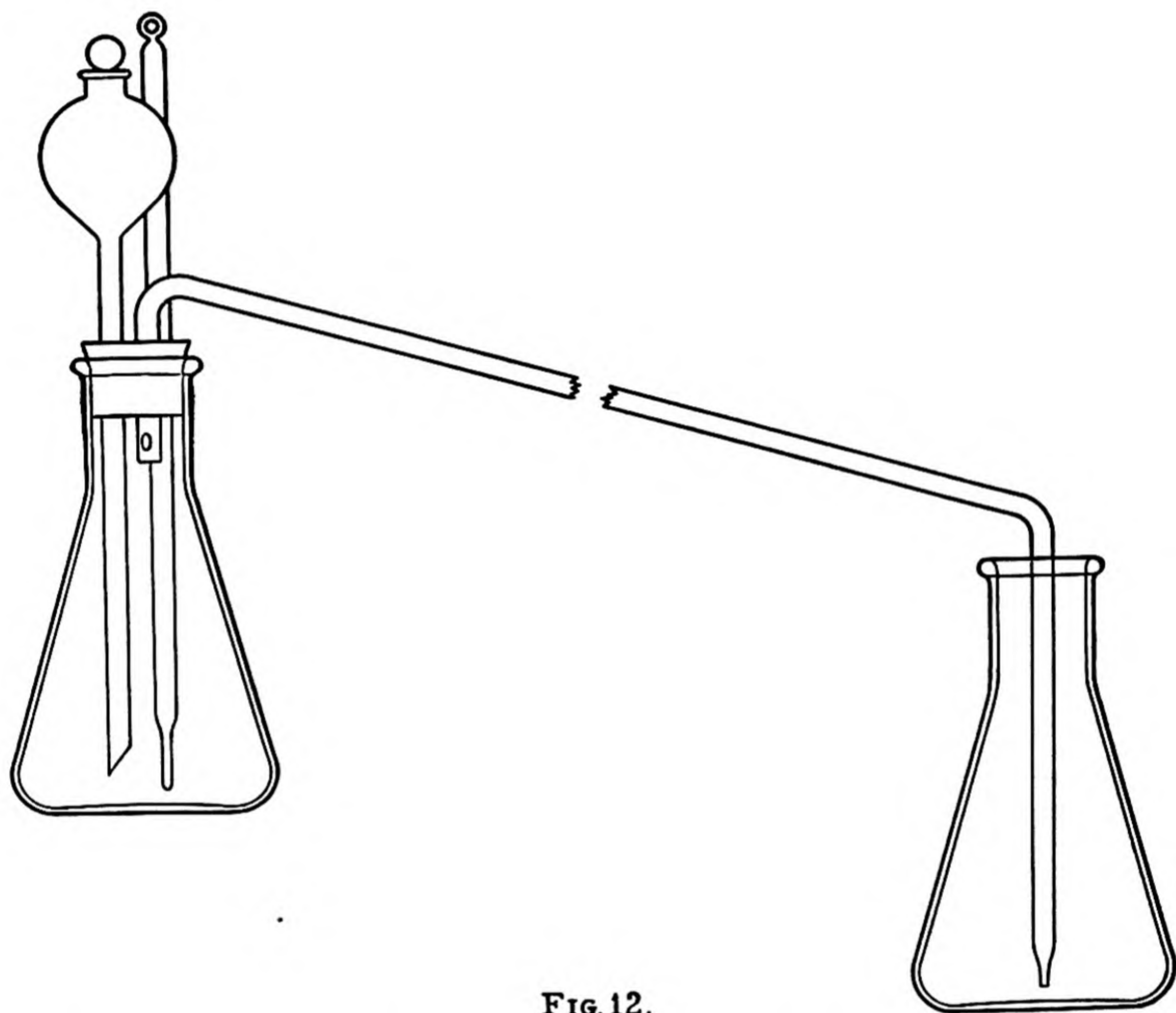


FIG. 12.

If the temperature during the distillation should rise above 108° C. at any time, some antimony (if present) may accompany the arsenic. Antimony may be detected in the distillate by the test given in Chapter I, No. 2 a.

c. *Volumetric Determination.* Cool the distillate, add a few drops of phenolphthalein solution as indicator, and make slightly alkaline with 20 per cent sodium hydroxide solution, then reacidify slightly with hydrochloric acid. Cool again, if at all warm. To the cold, slightly acid solution, add 3-4 grams, or an excess, of sodium

acid carbonate² and then a little starch solution. Titrate with standard iodine solution to a permanent blue tinge. See Chapter XXXIII for the preparation and standardization of the iodine solution. When the end of the titration is near, the color produced by the iodine will fade slowly after each addition of a drop. Proceed cautiously at this point until the addition of a single drop produces a permanent blue tinge. Multiply the milliliters of iodine solution used by the percentage value of 1 ml. in arsenic to obtain the result.

d. *Gravimetric Determination.* Pass hydrogen sulfide gas into the strongly acid distillate until all the arsenic is precipitated as As_2S_3 . Filter through a small weighed Gooch crucible, and wash the precipitate alternately with alcohol and carbon disulfide, finishing with a wash with alcohol. If large amounts of sulfur appear to be present in the precipitation with hydrogen sulfide, the As_2S_3 should be dissolved in ammonium hydroxide, filtered, acidified with hydrochloric acid, and again precipitated with hydrogen sulfide. Dry the sulfide at 100°C ., cool, and weigh as As_2S_3 .

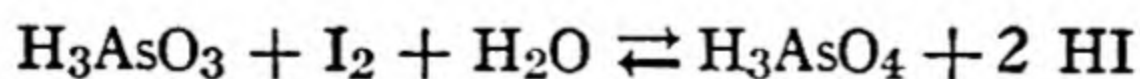
Multiply the weight of As_2S_3 by 0.6091 to obtain the weight of As.

II. HYDROGEN SULFIDE METHOD³

A. Application

The following method is similar to the preceding method except for the preliminary separation of the arsenic from the other elements present. The method is generally applicable and reliable with ores and metallurgical products.

² Before the sodium carbonate is added, the solution contains a slight excess of hydrochloric acid. The sodium salt neutralizes this, leaving solution acid with only CO_2 , together with an excess of the acid carbonate. The reaction during the titration may be expressed as follows:



The reaction is reversible, the presence of hydrochloric or hydriodic acid tending to make it proceed from right to left. The excess of sodium acid carbonate, which is otherwise without effect, neutralizes the hydriodic acid as fast as it is formed, so that the reaction proceeds completely from left to right. Free alkali is not permissible, as it causes reactions with the iodine.

³ A. H. Low, *J. Am. Chem. Soc.*, 28, 1715, 1906.

B. Interfering Elements

Only a few of the rarer elements such as germanium, selenium, tellurium, and possibly molybdenum are precipitated with the arsenic by hydrogen sulfide in strongly acid solution and are redissolved on treatment with sodium hydroxide.

C. Procedure

a. Treat 0.5 gram of the ore precisely as described for antimony in Antimony, I, C, a, and b. This will result in the arsenic being obtained on the filter as sulfide, the precipitate, flask, and delivery tube having been washed with the hydrochloric acid mixture to remove antimony.

b. Using hydrogen sulfide water,⁴ wash off the delivery tube into the flask, and then set it aside temporarily. Now wash out the flask six or seven times with hydrogen sulfide water, pouring over the precipitate in the funnel and allowing the filter to drain completely between washes. This is to remove most of the hydrochloric acid. If a very little acid remains it will do no harm. Reject the filtrate.

Place the flask, which may still contain adhering sulfide, under the funnel. Warm about 15 ml. of a 5 per cent solution of sodium hydroxide in a small beaker or wash bottle. Cleanse the delivery tube, held over the funnel, with a few drops of this, and then continue to run the solution very slowly over the precipitate to dissolve it. Use as little as possible (perhaps 10 ml., but more if necessary). Dilute about 5 ml. of the hydroxide solution with about 50 ml. of hot water for washing. Wash the filter six or seven times with this, but endeavor not to get a bulky filtrate, as it has to be boiled away.

Add to the solution in the flask about 2 grams of anhydrous sodium sulfate and 6-7 ml. of strong sulfuric acid. Support the flask over a small free flame and boil down to small bulk; then, with the flask in a holder, run down to a melt, over a strong flame, as in the original decomposition, following the same precautions in the heating and cooling.

⁴ It is best to have this slightly acidulated with acetic acid.

Any small amount of hydrochloric acid present is expelled during the heating before the arsenious sulfide is decomposed, and therefore causes no loss of arsenic by volatilization as chloride.

Add 50 ml. of hot water to the cold residue in the flask, heat to effect solution, and then boil for a short time to expel any possible SO_2 . Now add 50 ml. of cold water and cool under the tap, to room temperature. Add a few drops of phenolphthalein solution as indicator and make slightly alkaline with 20 per cent sodium hydroxide solution, then reacidify slightly with hydrochloric acid. Cool, again, if at all warm. To the cold, *slightly* acid solution, add 3-4 grams, or an excess, of sodium acid carbonate and then a little starch solution. Titrate with standard iodine solution to a permanent blue tinge. When the end of the titration is near, the color produced by the iodine will fade slowly after each addition of a drop. Proceed cautiously at this point until the addition of a single drop produces a permanent blue tinge. Multiply the milliliters of iodine solution used by the percentage value of 1 ml. in arsenic to obtain the result.

III. PEARCE-LOW METHOD ⁵

A. Application

This method is not applicable to ores containing phosphorus, vanadium, molybdenum, tungsten, or chromium, as these elements form compounds with silver nitrate under the given conditions. If these elements are known to be present the arsenic may be separated from them by distillation or by hydrogen sulfide as in the preceding methods.

B. Interfering Elements

In addition to the above-mentioned elements, selenium, tellurium, and large amounts of chlorides or sulfates should be absent.

C. Procedure

a. Thoroughly mix 0.5 gram of the finely ground ore in a platinum dish or large porcelain crucible, with 5 grams of a mixture of equal parts of dry sodium carbonate and potassium nitrate. It is a good plan to reserve a portion of the mixed salts for use as

⁵ This method was originally developed by Dr. Pearce and Dr. Low in the laboratory of the Boston and Colorado Smelting Works, at Argo, Colorado.

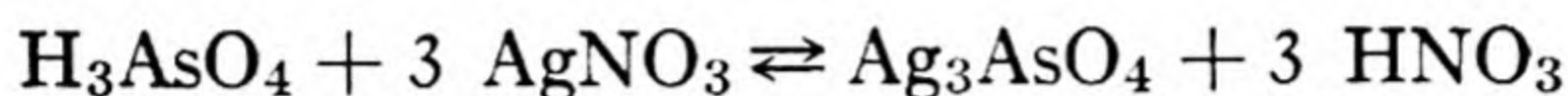
a cover. Heat the mass gradually over a Bunsen burner to complete fusion. It is best to use a very low flame at first and take plenty of time, so that the mixed salts will melt and soak through the mass before much decomposition occurs; in this way loss of arsenic is prevented with some ores that tend to lose arsenic by volatilization. Finally, heat to the full power of the Bunsen burner until thorough decomposition is effected. Prolonged heating over a blast lamp is sometimes necessary, especially with oxidized ores containing lead.

In testing heavy sulfide ores there is some danger of a loss of arsenic by volatilization during the deflagration. To avoid this proceed as follows: Cover the dish containing the weighed ore with a watch glass. Add a little nitric acid, and then heat gently, with the cover on, to complete dryness. The dish may be placed above a small free flame and the heat increased at the end. Allow to cool, loosen any splatterings on the cover with a moistened rubber-tipped glass rod, and rinse them into the dish with as little water as possible. It is usually unnecessary to evaporate this water if the amount is small. Add the 5 grams of nitrate mixture, heat cautiously to dryness, and then fuse and proceed as follows:

b. The melted mass should finally present a smooth and homogeneous appearance if the dish or crucible is taken up in the tongs and given a circular movement. Cool, extract the soluble portion by heating with water until thoroughly disintegrated, and then filter and wash the residue with cold water. Receive the filtrate in an 8-oz. flask. Drop a bit of litmus paper into the flask, and then add nitric acid carefully until the solution is plainly acid, simply avoiding a large excess, but if a precipitate has formed always add enough acid to dissolve it. Now add a sufficient quantity⁶ of a solution of silver nitrate, which will usually cause a white precipitate of silver chloride, and then cautiously add ammonia until, if arsenic is present, a reddish precipitate of silver arsenate appears. If too much ammonia is added, the precipitate first formed will redis-

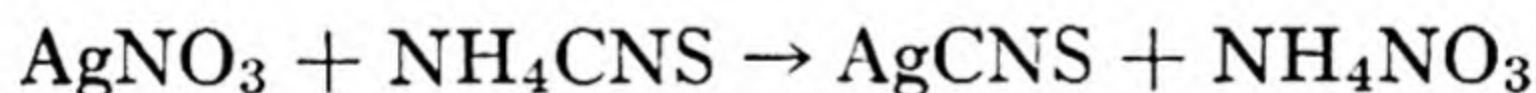
⁶ In order to avoid an unnecessarily large excess of silver nitrate, it is best to make up a solution containing, say, 17 grams in 500 ml. and use a definite amount. One milliliter of a solution of this strength will precipitate approximately 0.005 gram of arsenic, or 1 per cent if 0.5 gram of ore is taken for assay. Thus 10 ml. will usually be an excess. It is best to use at least 10 ml., however, as small amounts of arsenic may entirely fail to precipitate unless a considerable excess of silver nitrate is added.

solve and may not be observed at all. Then the bit of litmus paper in the liquid will show an alkaline reaction. Now cautiously add nitric acid (best dilute) until the red precipitate just redissolves or the litmus paper shows a slight acid reaction. To the faintly acid liquid add a few milliliters of a strong solution of sodium acetate or 1 or 2 grams of the crystals. This will effect a replacement of the free nitric acid, with acetic acid, and all the arsenic will be at once precipitated as silver arsenate, Ag_3AsO_4 .



Heat the precipitated mixture to boiling, then cool to room temperature, allowing the precipitate to settle somewhat, and filter. If the first portions run through turbid, return them to the filter once more. Test the filtrate with a little more silver nitrate and sodium acetate. Wash the precipitate with cold water until a portion of the washings shows only a faint cloud when tested for silver with a soluble chloride.

Now place the original flask under the funnel and dissolve the arsenate on the filter with cold dilute (1 : 1) nitric acid; 5 or 10 ml. will usually suffice. Wash the filter thoroughly with cold water. A white residue of silver chloride usually remains undissolved. Dilute the filtrate, if necessary, to about 100 ml., add about 5 ml. of a strong solution of ammonioferric alum, and titrate to a permanent red tinge with a solution of ammonium thiocyanate (Volhard), shaking well, especially at the end, to break up the clots of precipitate and free any solution held mechanically.



Multiply the number of milliliters required, by the arsenic value of 1 ml., to obtain the amount of arsenic in the ore.

See Chapter XXXIII for the preparation and standardization of the thiocyanate solution.

D. Modifications

*Sodium Carbonate and Zinc Oxide Method for Ores, etc.*⁷

For an arsenic determination, when antimony is not also required, this method is shorter and simpler than those previously

⁷ W. C. Ebaugh and C. B. Sprague, *J. Am. Chem. Soc.*, **29**, 1475, 1907.

described, but is inapplicable to oxidized ores containing much lead, as some of the arsenic always combines with the lead and fails to be extracted. Elements that precipitate with silver nitrate interfere; antimony does not.

Thoroughly mix 1 part of dry sodium carbonate and 4 parts of zinc oxide. Weigh 0.5 gram of the ore into a platinum dish and intimately mix it with 3 grams of the above mixture, then cover with 2 grams more. Partly cover the dish with a thin piece of asbestos board, so as to keep in the heat, and heat over a Bunsen burner to bright redness for about twenty minutes. An uncovered porcelain dish may be used, similarly heated in a muffle. Allow to cool, and transfer the mass to a suitable beaker, rinsing out the dish with hot water and making up the bulk in the beaker to about 50 ml. Heat the mixture to boiling, stirring well, and filter, washing thoroughly with hot water. The arsenic is in the form of soluble sodium arsenate. Receive the filtrate in an 8-oz. flask. Drop a small bit of litmus paper into the solution as an indicator, and then make slightly acid with acetic acid. Now add an excess of silver nitrate solution, as described in C, b, and agitate the mixture occasionally for a few minutes without heating. Filter the silver arsenate, refiltering if any runs through, and finish the determination as described in C, b.

BARIUM MINERALS

Mineral Name	Chemical Formula	% BaO	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Barite.....	BaSO ₄	65.7	White or tinted. Distinguished by high specific gravity	4.5	Ca, Sr, Fe, Si, F, Mg, Pb, Zn, S	Insol.	Na ₂ CO ₃
Witherite.....	BaCO ₃	77.7	Same	4.3	Same	HCl	Same
Barytocalcite.....	BaCO ₃ ·CaCO ₃	51.5	Same	3.6	Same	HCl	Same

Barite is commonly encountered in the insoluble residue from the acid digestion of ores of arsenic, antimony, lead, copper, zinc, manganese, and silver. Other barium minerals, principally silicates, borosilicates, or phosphates of aluminum and calcium, may be encountered occasionally.

CHAPTER V

BARIUM

I. SULFATE METHOD FOR ORES

A. Application

The following method gives good results on practically all types and grades of ores.

B. Interfering Elements

Calcium and strontium are the main interferences, owing to the insolubility of their sulfates. Strontium rarely occurs in sufficient quantity to cause a serious error in commercial analyses. If much calcium is present, the final precipitate of barium sulfate will be contaminated and should be fused and reprecipitated.

If large amounts of lead and silver are present, the analyst is cautioned to be careful that they are entirely removed from the insoluble residue before conducting a fusion in platinum ware.

C. Procedure

a. Decompose 0.5 gram (or suitable amount according to the grade of the ore) in a 4-oz. Erlenmeyer flask or a covered beaker, by one of the methods described for Insoluble Residue (Chapter XXIV), depending on its nature.

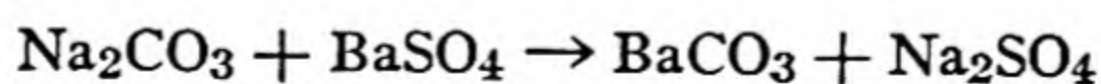
When solution is as complete as possible, add a few drops of strong sulfuric acid to make sure that all the barium will be rendered insoluble. Dilute the mixture with about 50 ml. of water, add a little paper pulp, heat to boiling, and filter, washing with hot water. Silver will be precipitated as the chloride in the usual digestion and may be removed by washing the residue with a warm dilute solution of ammonia. If the ore contains lead, add about 5 grams of ammonium chloride before boiling and filtering, in order to retain it all in solution.¹

¹ The ammonium chloride forms a soluble double salt with lead sulfate.

Place the filter and insoluble residue containing the barium in a platinum dish or crucible, and ignite to burn off the filter paper. Mix the cold residue with 3-5 grams of mixed sodium and potassium carbonates,² and fuse for a short time to convert the barium to carbonate. After cooling, heat the melt with water until disintegration is complete. For color indications of other elements see **Chapter II, No. I, C, a**. If a platinum dish has been used it will probably hold sufficient water for the purpose; a platinum crucible may be placed in water in a beaker. Filter, washing with dilute ammonia water³ until all sulfates are removed. The filtrate may be tested from time to time by catching a drop from the end of the funnel with a glass stirring rod and touching it to a drop of slightly acidified barium chloride solution on a black spot plate. When no white precipitate of barium sulfate forms, the washing is sufficiently complete.

b. Rinse the more or less impure barium carbonate on the filter, as completely as possible, into a small beaker. Some barium carbonate will still remain on the filter, and there may also be a little adhering in the dish or crucible used for the fusion. Dissolve this in 5 ml. of strong hydrochloric acid and then transfer to the beaker containing the bulk of the carbonate, covering at once with a watch glass to avoid loss by spattering. Warm the solution, wash off the cover and remove it, and then pour the liquid through the filter last used, so as to dissolve whatever barium carbonate was left there. Wash beaker and filter with hot water, and receive the filtrate in a large beaker. Dilute to about 300 ml., heat nearly to boiling, and add 10 to 30 ml. of 10 per cent sulfuric acid by means of a capillary funnel. Cover the beaker and allow to stand until cold, or best, over night, to insure the complete precipitation of the barium sulfate. Finally filter through a double paper and wash well with hot water. The precipitate is very fine and is liable to run through. It is safest to decant carefully through the filter without disturbing the precipitate in the bottom until most of the clear liquid is gone, then remove the beaker containing the filtrate and replace it with

² The mixed carbonates are used simply because the mixture fuses more easily than either of the single salts.



³ Barium carbonate is less soluble in water containing ammonia than in pure water.

another, so that if the barium sulfate runs through there will be less liquid to refilter. Always rub out the beaker with a rubber-tipped glass rod. The moist precipitate and filter may be ignited together over a Bunsen burner in a weighed platinum or porcelain crucible. The strong heat of a blast lamp should not be employed. The carbonaceous matter of the filter may reduce some of the barium sulfate to sulfide, but ignition with free access of air will easily effect reoxidation. The ignited barium sulfate should be perfectly white. The weight of the BaSO_4 multiplied by 0.657 will give the corresponding weight of BaO , if that is required.

In rapid technical work it is usually sufficient to ignite the barium sulfate in a small clay "annealing cup," and, when cold, shake and brush it from the cup to the scale pan for weighing.

In smelter practice the barium is usually required to be reported as sulfate, and all the barium in the ore is considered to exist as sulfate.

II. RAPID METHOD

A. Application

The following method, though not so reliable, will frequently serve for technical purposes. Gangue minerals which are not broken up by hydrofluoric acid or which liberate elements that form insoluble fluorides must be absent. The method should be checked against the preceding method for the material under consideration.

B. Procedure

Having obtained the insoluble residue, including the barium sulfate as above, ignite it in a small platinum dish to burn off the filter paper, and then, after cooling, add a few milliliters each of strong hydrochloric and hydrofluoric acids, in the order named, and evaporate on the water bath nearly or quite to dryness. It is best to repeat the operation to insure the complete expulsion of the silicic acid.⁴ Finally, take up in hydrochloric acid, dilute with hot water, and filter. Wash the residue well with hot water, and then ignite and weigh as BaSO_4 as described above.

⁴ Hydrofluoric acid decomposes silicates, dissolving the silica, which subsequently volatilizes as silicon tetrafluoride, SiF_4 .

BERYLLIUM MINERALS

Mineral Name	Chemical Formula	% BeO	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Beryl.....	$3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	14.0	White or tinted	2.7	Fe, Mn, Ca, Na, Li, rare earths	Insol.	Na_2CO_3 , NaOH
Phenacite.....	$2\text{BeO} \cdot \text{SiO}_2$	45.5	White or tinted	3.0	Same + Al	Insol.	Same
Chrysoberyl.....	$\text{BeO} \cdot \text{Al}_2\text{O}_3$	19.8	White or tinted	3.8	Same + SiO_2	Insol.	KHSO_4

A few rare beryllium minerals, such as helvite, danalite, gadolinite, and trimerite, are partly decomposed by hydrochloric acid. Complete decomposition of silicates is ordinarily best obtained by fusion with sodium carbonate, the fusion being repeated for the more refractory minerals. Chrysoberyl is more easily broken up by repeated fusions with potassium or sodium pyrosulfate.

The minerals in powdered form offer no characteristic properties by which beryllium may be identified, but its presence may readily be detected by the semi-micro method described in **Chapter I, No. 5.**

CHAPTER VI

BERYLLIUM

I. SODIUM CARBONATE FUSION METHOD¹

A. Application

This is the most rapid and accurate method at present available for technical purposes. It is not very satisfactory for small amounts of beryllium, but even for them it may be used advantageously as a preliminary separation for the removal of the bulk of the aluminum.

B. Interfering Elements

Of the elements that precipitate with ammonium hydroxide, iron, titanium, zirconium, thorium, and the rare earths will accompany the beryllium unless previously separated. Uranium, chromium, phosphorus, and possibly vanadium, not removed by the extraction of the sodium carbonate melt, will be caught in the ammonium hydroxide precipitate and counted as BeO when the beryllium is determined by difference.

C. Procedure

a. Treat 0.5 gram of the ore as described in the Indirect Method for Aluminum, Chapter II, I, C, a and b. It is not necessary to weigh the combined oxides.

b. Fuse the ignited oxides of beryllium, aluminum, iron, etc., in a platinum crucible with 5 grams of sodium carbonate. Place the cooled crucible and melt in a 400-ml. beaker containing about 100 ml. of hot water, and digest until the fused mixture is loose from the crucible. Remove the crucible and wash with a fine stream of hot water. Continue the digestion until the melt is completely disintegrated, breaking any lumps with a flattened glass rod if necessary. Finally bring to a boiling temperature and then remove from the hot plate and allow to cool. Filter, and wash with a 5 per cent solution of sodium carbonate. If the filtrate is yellow, uranium

¹ Wunder and Wenger, *Z. anal. Chem.*, 51, 470, 1912.

may be present. Dry the paper and precipitate, ignite, and repeat the fusion and extraction. Two fusions and extractions serve to remove the aluminum in most analyses; if the precipitate is bulky a third treatment is sometimes advisable.

c. Dry the final precipitate and paper, and ignite to the oxides. Fuse the ignited oxides with 2 or 3 grams of potassium bisulfate in a silica crucible. Dissolve the cooled melt in 50 ml. of water containing 5 ml. of hydrochloric acid and a little bromine water. Nearly neutralize the acid solution with sodium hydroxide, warm the solution, and pour it slowly with rapid stirring into 100 ml. of a warm 10 per cent solution of sodium hydroxide contained in a 400-ml. beaker. Filter on a rapid paper, wash with hot water, and reserve the filtrate. Dissolve the precipitate in a little hydrochloric acid, nearly neutralize with sodium hydroxide, and repeat the precipitation with sodium hydroxide. Filter through the same paper, catching the solution in the same beaker with the first filtrate. Wash well with hot water. Acidify the filtrate with hydrochloric acid, add 5 grams of ammonium chloride, and make just alkaline with ammonium hydroxide, using methyl red as an indicator. Add 2 drops of ammonium hydroxide in excess, heat to boiling, and filter the beryllium hydroxide on an ashless paper. Wash with a hot 2 per cent solution of ammonium nitrate. Dissolve the precipitate in hydrochloric acid and repeat the precipitation with ammonium hydroxide to remove alkali salts. Dry and ignite the precipitate in a porcelain crucible, cool in a desiccator, and weigh as BeO.

In accurate analyses, the BeO may be corrected for small amounts of aluminum by precipitation of the aluminum by 8-hydroxyquinoline.

Small amounts of beryllium lost with the aluminum in the extraction may be accurately determined with quinalizarin by Fischer's ² colorimetric method.

D. Modifications

a. A more rapid method but subject to more interfering elements is as follows:

Dissolve the precipitate from the sodium carbonate extractions in C, b in hydrochloric acid. This is best done by breaking up

² H. Fischer, *Z. anal. Chem.*, 73, 54, 1928; or Mitchell and Ward, *Modern Methods in Quantitative Analysis*, Longmans, Green & Co., 1932.

the filter paper and precipitate in a small beaker with a glass stirring rod and 10 ml. hydrochloric acid. Dilute to 100 ml. and precipitate with ammonium hydroxide, using methyl red as an indicator, and observing the same precautions in regard to an excess as with aluminum. Heat to boiling, and filter on an ashless paper. Redissolve and reprecipitate the hydroxides to make sure of removing all alkali salts. Wash the precipitate with 2 per cent ammonium nitrate solution, dry the precipitate and paper, ignite, and weigh as $\text{BeO} + \text{Fe}_2\text{O}_3$. Fuse the weighed oxides with potassium bisulfate in a silica crucible. Dissolve the melt in dilute sulfuric acid, and determine the Fe_2O_3 present by a volumetric or colorimetric method. See Chapter XV. Determine the BeO by difference.

b. Another procedure, which will take care of iron, titanium, vanadium, zirconium, thorium, and small amounts of the rare earths, is to dissolve the potassium bisulfate melt obtained in D, a in 10 per cent sulfuric acid, and, after cooling, to precipitate the iron, etc., with a cold 6 per cent water solution of cupferron. Stir in a little paper pulp and filter. Wash with a 2 per cent sulfuric acid wash solution containing a little cupferron. Carefully dry, char, and ignite the precipitate and paper. Weigh the combined oxides and obtain the BeO by difference as before.

c. Uranium may be separated by potassium ferrocyanide.³ The sulfuric acid solution obtained in C, c, or D, a and b, is neutralized with ammonium hydroxide, made very slightly acid with sulfuric acid, and the uranium precipitated with potassium ferrocyanide. Paper pulp is stirred in and the precipitate of uranium ferrocyanide with more or less iron is filtered off on a close paper. The beryllium is recovered from the filtrate by precipitation with ammonium hydroxide. Schoeller recommends the addition of tannin to the ammonium hydroxide solution.⁴

³ Schoeller and Webb, *Analyst*, 61, 235, 1936.

⁴ W. R. Schoeller, *The Analytical Chemistry of Tantalum and Niobium*, Chapman & Hall, Ltd., 1937.

BISMUTH MINERALS

Mineral Name	Chemical Formula	% Bi	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Bismuthinite.....	Bi_2S_3	81.2	Lead gray, metallic luster	6.5	Cu, Pb, Zn, Fe, As, Sb, Sn, Au, Ag, W, Mo, Ni, Co	HNO_3	
Native bismuth....	Bi	Silver white with reddish cast	9.8	As, S, Te, Ag, Pb, Zn	HNO_3	
Bismite.....	$\text{Bi}_2\text{O}_3 \cdot n\text{H}_2\text{O}$	Variable	White to straw yellow; earthy	3.4	Same as above	HCl, HNO_3	
Bismutite.....	$\text{Bi}_2\text{O}_3 \cdot \text{CO}_2 \cdot n\text{H}_2\text{O}$	Variable	White to greenish, yellowish, or grayish; earthy	7.0	Same as above	HCl, HNO_3	

Most of the bismuth minerals contain the bismuth in combination with lead (beegerite, lillianite, rezbanyite, bismutoplagonite, cosalite, galenobismutite, etc.); copper (aikinite, benjaminite, emplectite, klapprotholite, wittichenite, cuprobismutite, etc.); or silver (alaskite, aramayoite, matildite, schapbachite, schirmerite, etc.). Bismuth is combined with selenium and tellurium in the minerals guanajuatite and tetradymite. The above minerals are all sulfides, decomposed by nitric acid, and gray to black when pulverized.

Bismuth, like antimony and tin, precipitates basic salts from acid solutions upon dilution.

CHAPTER VII

BISMUTH

I. GENERAL METHOD FOR ORES

A. Application

The following procedure is applicable to almost all types and grades of ores containing bismuth in amounts determinable gravimetrically.

B. Interfering Elements

Large amounts of lead removed as the sulfate, or large amounts of silver removed as the chloride, will carry out small amounts of bismuth. If these separations are used double precipitations should be made. Moderate amounts of these elements do not interfere seriously in most technical analyses.

Elements that hydrolyze readily or precipitate as chlorides in weak acid solutions such as antimony, tin, silver, monovalent mercury, or monovalent thallium, will contaminate the precipitate of BiOCl .

C. Procedure

a. Treat 0.5 gram of the finely ground ore in an 8-oz. flask with 6-10 ml. of strong nitric acid, and boil gently, nearly to dryness. Add 10 ml. of strong hydrochloric acid, or more if necessary, and warm until solution is as complete as possible. A white curdy precipitate shows the presence of considerable silver. Remove from the heat and add (cautiously) 8 ml. of strong sulfuric acid. With the flask in a holder, boil over a free flame to strong sulfuric acid fumes. Allow to cool.

Add 25 ml. of water and boil gently for a short time to insure solution of all the bismuth sulfate, then cool quickly under the tap and filter, washing with dilute (1 : 10) sulfuric acid. Do not allow to stand long before filtering, or some basic bismuth sulfate may separate.

If large amounts of lead are present, the sulfuric acid may be omitted and the solution evaporated to a syrupy consistency. Evaporate twice to a small quantity with 10-ml. portions of hydrochloric acid to remove the nitric acid. Finally, add 10 ml. hydrochloric acid and 25 ml. water, heat to boiling, and filter. Wash the insoluble residue well with 1 : 1 hydrochloric acid.

Dilute the filtrate to about 100 ml., and make tests for antimony and tin by the methods given in Chapter I, No. 2 a, and No. 34 a.

b. Pass in hydrogen sulfide gas to saturation. Bismuth, copper, arsenic, antimony, etc., are precipitated as sulfides. Filter, washing with hydrogen sulfide water.

Rinse the precipitate as completely as possible into a beaker, add 3-4 grams of pure potassium cyanide, and warm gently for some time. Bismuth sulfide will remain undissolved, also cadmium sulfide, if present, and any lead (as sulfide) that may not have been removed as sulfate. Copper, silver, arsenic, antimony, and tin sulfides are dissolved. In the absence of arsenic, antimony, and tin, the potassium cyanide digestion may be omitted. Silver will usually be removed along with the insoluble residue.

Filter through the same filter as before, in order to act upon the traces of sulfides that could not be washed into the beaker. Wash with hot water.

Spread out the filter on a watch glass, and rinse off the sulfides into a beaker with hot water. To any residue adhering on the filter add a little dilute (1 : 2) nitric acid and warm until dissolved, then rinse into the main portion. Add a little strong nitric acid to the mixture in the beaker, if apparently necessary, and warm until all the bismuth is in solution and the separated sulfur is clean. Mercury sulfide is not dissolved by dilute nitric acid. Dilute somewhat and then filter, washing thoroughly with 1 : 2 nitric acid.

c. Dilute the filtrate, contained in a large beaker, to about 300 ml., and heat to boiling. Remove from the heat, and, to the hot solution, add dilute ammonia (one-third strong ammonia and two-thirds water) very cautiously, finally drop by drop, until the free acid is neutralized and the liquid remains faintly opalescent. There should not be a visible precipitate, but just a faint cloudiness. If the amount of bismuth is very small, this point may be difficult to

observe, in which case drop in a bit of litmus paper, and, working with dilute nitric acid and dilute ammonia, make the solution just faintly alkaline. Now add 1 ml. of dilute hydrochloric acid (1 : 3). The opalescent mixture will clear for an instant, and then, with an appreciable amount of bismuth present, a white crystalline precipitate of bismuth oxychloride, BiOCl , will form.

Maintain the liquid hot, but not boiling, for about an hour, to allow the precipitate to separate and settle; then filter on a weighed Gooch filter and wash thoroughly with hot water.

Dry the residue at 100°C . to constant weight. Multiply the weight of BiOCl found by 0.8024 to obtain the weight of the bismuth.

D. Modification

Instead of the bismuth being precipitated as basic chloride, it may, in the absence of lead, thallium, cadmium, and mercury, be precipitated as basic carbonate, as follows:

Partly neutralize the filtrate from the solution of the bismuth sulfide in nitric acid, C, b, with ammonia, but without producing any permanent precipitate, then add a solution of ammonium carbonate in slight excess and heat to boiling. Maintain at nearly boiling temperature for some time, until the bismuth carbonate has settled well; then filter, washing well with hot water.

Dry the precipitate and transfer it as completely as possible from the paper to a small weighed porcelain crucible. Burn the paper carefully, and add the ash to the precipitate in the crucible. Ignite the whole at a low red heat, cool, and weigh as Bi_2O_3 . Multiply the weight found by 0.8970 to obtain the weight of the bismuth.

A better procedure, if the amount of the precipitate is small, is to dissolve it on the filter with hot dilute acid, receiving the filtrate in a weighed platinum dish. Evaporate the filtrate to dryness, then ignite, gently at first, but finally to bright redness. Weigh as Bi_2O_3 , as before.

Also, if the precipitate is large in amount, most of it may, after drying, be removed to a watch glass. Dissolve what still adheres to the filter as just described, and evaporate the solution to dryness. Now add the main portion of the precipitate and ignite as before.

The oxidation of the bismuth sulfide by nitric acid may produce some bismuth sulfate; this would cause slight contamination of the basic bismuth carbonate with basic sulfate, which would fail to be converted to oxide on ignition. The error thus introduced is ordinarily sufficiently small to be negligible in technical work.

II. DOCIMASTIC METHOD

A. Application

This method is for bismuth in refined lead, lead bullion, or ores containing only a few tenths of a per cent of bismuth. With ores containing 2-3 per cent, it is better to treat 0.5 gram without running into a lead button.

B. Interfering Elements

The lead button obtained by the fire assay will contain all the silver and bismuth and may be contaminated with more or less copper, arsenic, antimony, tin, and zinc. The lead button should be soft and bright with iridescent top when poured, free of slag, into an open mold. Arsenic, antimony, copper, and zinc, when present in the button in appreciable amount, cause the button to be brittle and lusterless. Arsenic may usually be detected during the fusion by the dense white fumes rising from the crucible; copper gives a characteristic green to black slag often containing red streaks.

C. Procedure

a. Run down 10 grams of the ore with sufficient litharge and the necessary fluxes to produce a 10-gram lead button. A good charge consists of 75 grams of litharge, 30 grams of sodium carbonate, 15 grams of borax glass, and flour or niter to give the proper oxidation or reduction conditions to produce a 10-gram lead button. Roll the lead button into a ribbon, and dissolve it in a mixture of 25 ml. of nitric acid and 50 ml. of water, by warming.

b. For lead bullion or refined lead, dissolve 25 grams of the lead, best rolled or hammered out thin and cut into small pieces, in a mixture of 250 ml. of water and 40 ml. of nitric acid of 1.42 sp. gr., using a large covered beaker.

c. To the hot solution from a and b add dilute ammonia (1 : 2), very cautiously, finally drop by drop, until the free acid is neutral-

ized and the liquid remains faintly opalescent. There should not be a visible precipitate but just a faint cloudiness. Now add 1 ml. of dilute hydrochloric acid (1 : 3). The solution will clear for an instant, and then, if any considerable amount of bismuth is present, a crystalline precipitate of bismuth oxychloride will form. Again place the beaker over the heat so that the liquid will keep hot but not boil. In an hour the bismuth oxychloride, together with a little lead, will have settled. Filter off the precipitate, and wash it once or twice with boiling water. In addition to bismuth and lead, the precipitate may contain some antimony, if any appreciable quantity is present in the sample.

Dissolve the precipitate on the filter in a small quantity of hot dilute hydrochloric acid (1 : 3), wash the filter with hot water and dilute the filtrate with water, taking care not to make the liquid so dilute as to cause a precipitation of the bismuth as basic chloride. Pass hydrogen sulfide into the liquid to precipitate all the bismuth, lead, and antimony as sulfides, filter, wash once with water and twice with warm ammonium sulfide to dissolve the antimony sulfide, and then, after washing once more with water, dissolve the precipitate of bismuth and lead sulfides by placing filter and contents in a small beaker and heating with dilute nitric acid (1 : 4). Boil so as thoroughly to disintegrate the filter paper, and then dilute somewhat with hot water, and filter. Wash the filter well, first with a little warm dilute nitric acid (1 : 4) and then with hot water. Partly neutralize the nitric acid in the filtrate with ammonia, dilute with warm water to a volume of about 300 ml., and then complete the neutralization and add 1 ml. of dilute hydrochloric acid as described above for the original precipitation. The bismuth will now come down as basic chloride free from lead. Filter on a weighed filter or Gooch crucible, wash well with hot water, dry at 100° C., and weigh as BiOCl . This weight multiplied by 0.8024 will give that of the bismuth.

d. In the absence of appreciable amounts of antimony, the precipitation by hydrogen sulfide and subsequent washing with ammonium sulfide may be omitted, as only a small portion of whatever antimony is present is precipitated with the bismuth. Then the first precipitate, containing the bismuth and a little lead, may be at once redissolved on the filter with warm dilute nitric acid (1 : 4) and the

precipitation repeated on the filtrate as described. Copper, silver, arsenic, and such amounts of iron as occur in refined lead do not interfere.

III. VOLUMETRIC METHOD

A. Application

This procedure is desirable for ores containing appreciable amounts of bismuth or for bismuth in bismuth bullion.

B. Interfering Elements

As this method is simply a continuation of the oxychloride method, the same interferences apply.

C. Procedure

a. For bullions containing bismuth up to 25 per cent, weigh out 10 grams and dissolve in 15 ml. of nitric acid.

From 25 to 50 per cent, 5 grams in 10 ml. of nitric acid.

Over 50 per cent, 2 grams in 10 ml. of nitric acid.

Weigh the determined amount into a 600-ml. beaker. Add 50 ml. of water and the required amount of nitric acid plus 1 gram of tartaric acid. Warm until dissolved, and then dilute to 500 ml. with hot water. Boil the solution and add 5 ml. of 85 per cent phosphoric acid solution, previously somewhat diluted. Continue the boiling for five to ten minutes, and then allow to settle in a warm place. Filter on a close paper, washing two or three times with hot water. Dissolve the precipitate through the filter into the original beaker with hot dilute (1 : 1) hydrochloric acid. Be sure that none of the bismuth salt remains in the paper. Neutralize the filtrate with ammonia, cautiously, until a faint permanent cloud is produced. Now add 1 ml. of 1 : 1 nitric acid and dilute to 500 ml. with hot water. The bismuth precipitates as BiOCl . Allow to settle overnight in a warm place, and then filter on a close paper, washing thoroughly with hot water until free from soluble chlorides.

b. For ores, follow the procedure for the determination of bismuth as the oxychloride in I, C, a, b, and c.

c. Dissolve the precipitate of BiOCl from a and b through the filter with hot 1 : 1 nitric acid, washing the paper well with the same acid but not using an undue excess. Receive the filtrate in a 250-ml.

flask. Cool completely, and then, from a buret, run in an excess of the standard silver nitrate solution. Shake well to coagulate the silver chloride, and then titrate the excess of silver nitrate solution with the standard ammonium thiocyanate solution, with ferric alum as indicator (see **Chlorine, III, C**).

This shows the number of milliliters of silver solution consumed by the bismuth, from which the percentage may be calculated.

CADMIUM MINERALS

Mineral Name	Chemical Formula	% Cd	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposition by	
						Acid	Flux
Greenockite	CdS	77.7	Orange-yellow to brick red, earthy	5.0	Zn, Fe, Mn, Hg, Pb, Cu, Ag, Au, Ca, Mg, Sn	HCl	

The determination of cadmium is confined chiefly to the analysis of zinc ores, flue dust, calcines, spelter, and products of electrolytic and concentrating processes.

CHAPTER VIII

CADMIUM

I. METHOD FOR ORES OR FLUE DUST

A. Application

This method gives good results in the presence of moderate amounts of associated elements. Care must be taken to make clean separations from the other elements precipitated by hydrogen sulfide in acid solution. The separation of cadmium from zinc requires careful regulation of the acidity.

B. Interfering Elements

Zinc, silver, lead, copper, bismuth, arsenic, and antimony, the elements most frequently encountered, precipitate with the cadmium as sulfides. Mercury, molybdenum, tin, and the other members of the H_2S group are seldom present.

C. Procedure

a. To 0.5 gram (or appropriate amount) of the material in a 150-ml. beaker add 10 ml. of strong hydrochloric acid and 5 ml. of strong nitric acid. Boil until any sulfides present are decomposed and the acid is perhaps half expelled. If oxides still remain, continue to heat with addition of hydrochloric acid until the solution is as complete as possible. Finally, add about 6 ml. of strong sulfuric acid and boil, until fuming copiously. Practically all the arsenic will be lost during the digestion. Cool, add about 25 ml. of water, heat to boiling, and allow to stand, hot, for a short time, to insure the solution of anhydrous iron sulfate, etc. Then cool, filter off the insoluble residue (including any lead sulfate), and wash with cold dilute sulfuric acid (1 : 10). The presence of copper may be recognized, at this point, by the color of the solution.

Neutralize the filtrate with ammonium hydroxide, and add exactly 15 ml. of sulfuric acid. Dilute to 100 ml., add 5 grams of ammonium sulfate,¹ and pass in hydrogen sulfide gas to saturation. Add 25 ml. of water and continue the treatment with hydrogen sulfide for 5 to 10 minutes longer. Stir in a little paper pulp, and filter off the precipitated sulfides. Wash with dilute hydrogen sulfide water slightly acidulated with sulfuric acid.

b. Rinse the precipitate from the filter into a beaker as completely as possible, using no more water than necessary, place the beaker under the funnel, and pour through the filter a strong solution of pure potassium cyanide. Agitate the beaker so as to mix the liquids, using no more cyanide solution than is necessary to dissolve the soluble copper sulfide, etc., that may be present. If no bismuth or lead is present (any lead should have been practically all removed as sulfate), the cadmium sulfide will now appear yellow or orange.² Filter the mixture through the same filter as before. If it runs through turbid, return it through the filter until clear. Wash well with dilute hydrogen sulfide water. The cadmium sulfide has a tendency to pack on the filter and impede filtration. If possible, wash it loose each time, and the washing will then proceed much more rapidly. If the washed precipitate appears appreciably discolored, indicating bismuth, proceed as in d, below. If clean and yellow or orange, dissolve it by pouring through the filter hot dilute (1 : 1) hydrochloric acid, using as little as possible. Carefully add about 5 ml. of sulfuric acid and take to fumes on the hot plate. If the solution turns brown from carbon introduced through filter paper or pulp, a few drops of nitric acid (add cautiously) and continued fuming will clear it. Cool and dilute to about 100 ml.

c. Neutralize the solution with ammonia; add 10 grams of ammonium sulfate and exactly 30 ml. of sulfuric acid. Dilute to 200 ml. and pass in hydrogen sulfide gas to saturation. Increase the volume to 250 ml. while continuing the passage of hydrogen sulfide. Add a little paper pulp, and filter off the cadmium sulfide. Test the filtrate for zinc by neutralizing slowly with ammonia. If much

¹ The presence of a large amount of ammonium sulfate is essential for good results in precipitating cadmium with hydrogen sulfide from a sulfuric acid solution.

² When precipitated from sulfuric acid solutions, unless very weak in acid, the cadmium sulfide is orange rather than pure yellow.

white zinc sulfide is precipitated the cadmium sulfide should be dissolved and reprecipitated. Dissolve the final precipitate of cadmium sulfide in hot dilute hydrochloric acid (1 : 1), using as little as possible. If the volume of the filtrate is not too large, receive it in a large weighed porcelain crucible; otherwise collect it in a beaker and transfer it to the crucible in small portions at a time. Place the crucible and contents on a water bath and evaporate the solution of cadmium chloride to complete dryness. Now cover the crucible and add a slight excess of dilute sulfuric acid. When spattering has ceased, remove and rinse off the cover and continue the evaporation as far as possible on the water bath. Finally, remove the excess of sulfuric acid by cautiously heating over a free flame until no more fumes are evolved. Avoid heating higher than necessary. It is best to place the crucible within a larger one fitted inside with an asbestos ring, so that the crucibles do not touch. Or the crucible may be supported on a clay triangle on a small iron sand bath containing no sand, so that it just fails to touch the bottom. When the fumes have ceased to come off, cool and weigh the crucible and contents. The cadmium sulfate, CdSO_4 , should be pure white and soluble in water without residue. Its weight multiplied by 0.5392 will give the weight of the cadmium, from which the percentage may be calculated.

d. If the cadmium sulfide, after treatment with potassium cyanide, appears dark colored, bismuth or lead (possibly mercury) may be present. Place the moist precipitate and filter in an 8-oz. flask, and add 10 ml. of strong hydrochloric acid and the same amount of water. Boil the mixture until all the cadmium sulfide is dissolved, the hydrogen sulfide expelled, and the filter well disintegrated. Any dark insoluble residue apparently free from cadmium may be neglected. Dilute with 25 ml. of hot water, and filter, washing thoroughly with hot water. Dilute the filtrate somewhat; add sodium carbonate in slight excess and then 1 or 2 grams of potassium cyanide. Digest for some time at a gentle heat, and filter. Wash with cold water. Bismuth and lead remain on the filter as carbonates. Pass hydrogen sulfide through the filtrate, diluted if necessary. This should precipitate pure yellow cadmium sulfide unless mercury is present, which rarely happens. Filter, wash with hydrogen sulfide water containing several grams of ammonium ni-

trate (to prevent running through), and then dissolve in hydrochloric acid and finish as described above.

D. Modifications

a. When copper, silver, mercury, antimony, or bismuth is present in only small amount, it may be conveniently removed by reduction to the metal. Arsenic is volatilized as AsH_3 by the same operation. If the ore contains no copper, a few drops of a copper sulfate solution should be added as an aid in bringing down the other elements. To the sulfuric acid solution, obtained in C, a, add a strip of clean sheet iron or a gram of pure powdered iron and heat gently on the hot plate for about fifteen minutes. Add a little more iron to complete the reduction, and filter on a small paper. Treat the filtrate as in C, c.

b. The cadmium may be determined volumetrically after separating as the sulfide as described in C. Neutralize the hydrochloric acid solution of the clean cadmium sulfide with ammonium hydroxide, and make very slightly acid with hydrochloric acid. Titrate hot with standard potassium ferrocyanide, precisely as for zinc (Chapter XXXI). Standardize the ferrocyanide solution against C.P. cadmium sulfate.

II. ELECTROLYTIC METHOD

A. Application

Cadmium can be separated electrolytically in a satisfactory manner from its solution in various electrolytes. Its alkaline double-cyanide solution is perhaps as good as any, if not the best electrolyte. The method may be applied to an ore.

B. Interfering Elements

The interfering elements are the same as in the preceding method.

C. Procedure

a. Treat 1 gram of the ore by the method previously described until a solution of the chloride or sulfate is obtained, free from the other members of the hydrogen sulfide group. The solution should be evaporated if necessary, so as to have the volume well below 100

ml. Add a drop or two of phenolphthalein solution and then pure sodium or potassium hydroxide solution until a permanent red color is obtained. Now add cautiously a strong solution of pure potassium cyanide until the precipitated cadmium hydroxide is completely dissolved, avoiding an excess. Dilute to 100-125 ml., and, using the same beaker and electrodes as for copper (Copper II, C, b), electrolyze with a current of $ND_{100} = 0.04$ to 0.06 ampere and volts = 2.9-3.2. Keep the solution at a temperature of about 60° C. Usually the deposition is complete in four to six hours. Test by raising the level of the liquid slightly and noting whether any deposition occurs on the clean platinum surface during half an hour or so. When the operation is ended, disconnect and remove the electrode, wash it with hot water, then with alcohol, and finally dry it at 100° C., cool, and weigh.

It is a good plan to replace the electrode in the solution and electrolyze for another half hour. The electrode should first be cleaned with nitric acid, then washed, ignited, and again weighed. If desired, the solution can be tested with hydrogen sulfide. As this may produce a yellow color in the cyanide solution, even in the absence of cadmium, it is best first to acidify with hydrochloric acid (under a hood) and then heat until all the hydrocyanic acid is expelled.

b. Treadwell,³ using the same electrolyte, recommends electrolyzing in the cold for five to six hours with a current of 0.5-0.7 ampere and an electromotive force of 4.8-5 volts. At the end of this time the current is increased to 1-1.2 amperes and the solution is electrolyzed for an hour or more. Treadwell states that, unless the current is increased toward the end of the operation, not all the cadmium will be deposited at the end of twelve hours. If the stronger current is used from the beginning, some of the metal is likely to be deposited in a spongy form, resulting in a possible loss in washing.

III. CADMIUM IN SPELTER

A. Procedure

a. Dissolve 25 grams of the sample in a 400-ml. beaker in a mixture of 52 ml. of strong sulfuric acid and 200 ml. of water. With very pure zinc it may be necessary to add a few drops of

³ Treadwell, Hall, Analytical Chemistry, II, 8th ed., p. 197, John Wiley & Sons, Inc.

very dilute platinum chloride solution from time to time, to hasten the action. The above amount of acid is approximately 30 ml. more than is required to dissolve 25 grams of zinc, and therefore about 30 ml. of free acid will remain in the solution. Lead, copper, and probably a small amount of cadmium remain undissolved. Pay no attention to the flocculent residue, but be sure that all the zinc is dissolved.

b. Add 15 grams of solid ammonium sulfate to the warm liquid, and pass in hydrogen sulfide for ten minutes. Allow to stand warm for half an hour, and then again pass in hydrogen sulfide for ten minutes more. All the cadmium will be precipitated as sulfide, which will be mixed with considerable zinc sulfide, together with lead and copper. Filter through a 12.5-cm. paper, washing three or four times with warm water. The filtration is rather slow but proceeds steadily enough if a good column is established in the funnel stem. Return the precipitate, paper and all, to the beaker in which the precipitation was made; add 10 ml. of strong sulfuric acid and 10 ml. of strong nitric acid. Cover the beaker and heat it until sulfuric acid fumes are given off. Remove the beaker from the source of heat, and to the hot, but not strongly fuming, liquid add a few more milliliters of strong nitric acid. Again boil to fumes.

Repeat the addition of nitric acid as above, until the paper is completely consumed. This usually requires about three additions of the acid with intermediate fuming, the whole operation taking about three-quarters of an hour. It is important that the paper be completely oxidized.

c. Cool the solution, dilute to 50 ml. with cold water, then boil, cool, and allow to stand until the lead sulfate settles. Filter off the lead sulfate, and wash it once or twice with dilute sulfuric acid (1 : 10). The liquid now contains about 12 ml. of sulfuric acid in 100 ml. Add 5 grams of ammonium sulfate and pass hydrogen sulfide into the warm solution exactly as before. Cadmium comes down as sulfide practically free from zinc. Filter through a 9-cm. paper, and wash the precipitate three or four times with warm water.

d. Treat paper and precipitate in a No. 2 beaker with 5 ml. of sulfuric acid and 5 ml. of nitric acid, evaporating to fumes. Add

nitric acid as before to the hot liquid and again evaporate, repeating this procedure until the paper is destroyed. Now cool, add 5 ml. of cold water, and evaporate to fumes. Do this a second time. These last evaporations are to make certain of the expulsion of all nitric acid. The work should be done in a place free from heavy nitric fumes, since the presence of even a trace of nitric acid in the solution interferes with the subsequent electrolysis of the cadmium.

e. Add 25 or 30 ml. of water to the sulfuric acid residue, and heat until all soluble salts are dissolved. Cool, neutralize the excess of free sulfuric acid with ammonia (using litmus paper as an indicator), and then add 4.5 ml. of 1 : 2 sulfuric acid. This gives a solution containing 1.5 ml. of free sulfuric acid. Dilute with water to 125 ml. and electrolyze (preferably overnight), using a current of 0.1 ampere, 2.6 volts, to about 10 sq. in. of cathode surface (one side). The cathodes are perforated platinum cylinders, $2\frac{1}{8}$ in. high by $1\frac{1}{2}$ in. in diameter. Under the conditions given, cadmium is precipitated free from zinc, even if a trace of zinc remains in the solution. Copper also comes down with the cadmium. After weighing the cathode, dissolve the deposited metal in a few drops of nitric acid, dilute, boil, cool, and make alkaline with ammonia. Dilute to 10 ml., and compare the color with that of a similar solution containing a known amount of copper. The 0.2 or 0.3 mg. of copper usually present may be closely estimated in this way.

f. If the laboratory is not equipped with electrolytic apparatus, cadmium may be determined by weighing as sulfate. Since two precipitations with hydrogen sulfide, as described above, may not remove all the zinc (and will not unless the work is done with great care), a third precipitation with hydrogen sulfide should be made. This is unnecessary when the electrolytic method is used, because under the conditions given a small amount of zinc will remain in the electrolyte.

Wash the cadmium sulfide from the third precipitation with warm water, and then dissolve it in hot dilute nitric acid. Evaporate the solution to smaller bulk, cool, if necessary, and add 0.5 to 1 ml. of sulfuric acid. Evaporate to dryness in a weighed porcelain crucible, and finally ignite at a low temperature to constant weight. The resulting CdSO_4 is likely to contain copper. The

copper should be estimated colorimetrically, calculated to CuSO_4 , and deducted.⁴

Note that the presence of a large amount of ammonium sulfate is essential to good results in precipitating cadmium with hydrogen sulfide from sulfuric acid solutions. The proportions of acid and water are also important in getting clean separations. Those given above should be strictly adhered to.

⁴ The amount of copper present will probably not exceed 0.2 or 0.3 mg. Dissolve the residue in the crucible by warming with a little nitric acid, transfer the solution to a test tube, make ammoniacal to develop the blue color due to copper, and dilute to about 10 ml. Prepare a copper solution of known strength as follows: Dissolve exactly 100 mg. of pure copper foil in nitric acid, dilute somewhat, add an excess of ammonia, and then make the solution up to 100 ml.; 1 ml. = 1 mg. of copper.

From a buret, run some of this solution, say 1 ml., into a test tube similar to the first. Dilute to the same height as the liquid in the first test tube, and compare the color. Repeat the test with different amounts of the prepared copper solution, until the color of the first test tube is matched. From the amount of the prepared copper solution required, calculate the copper used. Calculate this to CuSO_4 and deduct the weight from the weight of the impure CdSO_4 before calculating the Cd.

CALCIUM MINERALS

Mineral Name	Chemical Formula	% CaO	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Calcite (aragonite).....	CaCO ₃	56.0	White or tinted	2.7	Mg, Si, Fe, Mn, Ti, Na, K, F, P, C, S, Ba, Cu, Pb, Zn, Sr	HCl	Na ₂ CO ₃
Dolomite.....	CaCO ₃ ·MgCO ₃	30.4	White or tinted	2.9	Same	HCl	Na ₂ CO ₃
Gypsum.....	CaSO ₄ ·2H ₂ O	32.5	White or tinted	2.3	Same	HCl	Na ₂ CO ₃
Anhydrite.....	CaSO ₄	41.2	Grayish white	2.9	Same	HCl	Na ₂ CO ₃
Fluorite.....	CaF ₂	51.1	White or tinted	3.2	Pb, Ag, Zn, Si, Ba, Sn, F, P, Mg	H ₂ SO ₄ , HClO ₄	Na ₂ CO ₃ Na ₂ CO ₃ + KNO ₃
Apatite..... (phosphate rock)	3 Ca ₃ (PO ₄) ₂ ·CaF ₂ 3 Ca ₃ (PO ₄) ₂ ·CaCl ₂	54-56	White to greenish or grayish	3.2	Si, Fe, Mn, Ti, Mg, Na, K	HCl, HNO ₃	Na ₂ CO ₃
Amphiboles..... (asbestos)	Complex silicates	White to gray or tinted, fibrous	2.9 to 3.2	Fe, Mn, Ti, Al, Na, K	Insol.	Na ₂ CO ₃

Calcium minerals are usually white or light colored when pulverized. The carbonates, sulfates, phosphates, borates, and nitrates are acid soluble, and a number of the silicates, such as the zeolites, anorthite, vesuvianite, and epidote, are decomposed by hydrochloric acid with a gelatinous residue. The minerals insoluble in acid are readily broken up by alkaline fusion.

CHAPTER IX

CALCIUM

I. VOLUMETRIC-OXALATE METHOD

A. Application

The following procedure serves very well for ores, limestone, cement, slags, and materials containing calcium in sufficient quantity to be determined volumetrically. Fluorspar, phosphate rock, and ores containing appreciable amounts of barium, strontium, tungsten, or vanadium, must be given special treatment.

B. Interfering Elements

Most technical methods allow only for the separation of those elements left insoluble by methods of decomposition, or by precipitation with ammonium hydroxide in the presence of bromine. Lundell and Hoffman¹ outline a great many possible interfering elements, the majority of which belong to the hydrogen sulfide or ammonium sulfide groups.

Strontium, when present, will be precipitated quantitatively and counted as calcium. Barium in small amounts does not interfere if double precipitations are observed. Tests for fluorine, phosphorus, barium, and strontium should be made on the material before starting the analysis. See Chapter I.

C. Procedure

a. Treat 0.5 gram of the ore in a 150-ml. beaker with whatever acids are best suited to decompose it. Begin ordinarily with 10 ml. of strong hydrochloric acid and heat gently. With carbonates, the acid should be added cautiously, the beaker being covered, to avoid loss by spattering. If sulfides are present, add 5 ml. of nitric acid

¹ Outlines of Methods of Chemical Analysis, John Wiley & Sons, Inc., 1938.

(after the oxides are dissolved) and boil gently until decomposed. If the decomposition is complete, sulfuric acid is unnecessary, and should be avoided unless carbon is believed to be present. With most ores a small amount of sulfuric acid is helpful in detecting the presence of barium, as barium interferes in the magnesium determination which practically always follows that of calcium. In any case, boil until most of the free acid is expelled, over a free flame if sulfuric acid has been used. If the sulfuric acid solution turns brown in color, carbon is present, and may be conveniently removed at this point by the careful addition of nitric acid and continued fuming. A green or blue-green color denotes the presence of copper, nickel, vanadium, chromium, or possibly manganese. Allow to cool, if necessary, add about 100 ml. of water and 5 ml. of strong hydrochloric acid, heat until the salts are dissolved, and then filter (never omit this if there is any appreciable amount of insoluble residue), washing with hot water.

Examine the insoluble residue. If not properly decomposed, leach with a little hot ammonium acetate solution to remove any lead sulfate, ignite the paper and residue in a platinum crucible, and fuse with sodium carbonate. Dissolve the melt in hydrochloric acid, dehydrate the silica, filter, and combine the filtrate with the filtrate obtained from the acid decomposition. Test the solution for the hydrogen sulfide and ammonium sulfide groups by the drop method, and proceed as in b, or c.

b. If the elements of the hydrogen sulfide and ammonium sulfide groups are absent, add a gram or two of ammonium chloride, 5-10 ml. of saturated bromine water, and a very slight excess of ammonia. Cover the beaker and boil until all free ammonia is expelled. Allow to settle somewhat and then filter through an 11-cm. filter and wash thoroughly with hot, dilute ammonium chloride solution² (2 per cent).

The above procedure renders the usual double precipitation of the iron entirely unnecessary. The usual retention of lime by iron appears to be due to the formation of calcium carbonate, by the absorption of carbon dioxide from the air in the presence of free

² Ammonium chloride is used to render any calcium carbonate which may be present more soluble. Calcium carbonate might be formed either from ammonium carbonate present in the ammonia, or by the absorption of carbon dioxide from the air.

ammonia, and this does not occur if the ammonia is expelled previous to filtration. Neglect to filter off the insoluble residue before the iron precipitation will usually produce a low result.

c. In the presence of members of the hydrogen sulfide group, pass hydrogen sulfide gas into the filtrate (from a) until saturated and allow the precipitate to coagulate and settle. Filter off the precipitated sulfides and wash with hydrogen sulfide water. Add a gram of ammonium chloride and a slight excess of ammonia to the filtrate, and continue passing in hydrogen sulfide gas until all the members of the ammonium sulfide group are precipitated. Filter, and wash with ammonium sulfide water. Boil the filtrate to expel the hydrogen sulfide gas, and reduce the volume. If sulfur separates out, it may be removed by oxidation with bromine water or hydrogen peroxide.

d. Adjust the filtrate from b or c, in a 400-ml. beaker, to a volume of 100 to 300 ml., according to the amount of calcium present. Make distinctly alkaline with ammonium hydroxide, heat to boiling, and add an excess of ammonium oxalate solution. This should be added in sufficient amount to convert all possible calcium and magnesium to oxalates (the magnesium oxalate remaining in solution). Thirty milliliters of a saturated solution should be sufficient. It is best to dilute it somewhat and add it boiling hot. Boil the mixture about ten minutes, allow to stand hot and settle, and then filter through an 11-cm. filter and wash well with hot water. For more exact work allow to stand overnight.

The mode of procedure now depends upon whether the ore contains much or little magnesium. If much, the calcium oxalate is almost sure to contain an appreciable amount of magnesium oxalate and should therefore be purified. Unless the amount of magnesium is known to be insignificant, it is always safest to proceed as follows:

Without troubling to wash the precipitated oxalate more than once, rinse it from the filter into the original beaker. What little remains adhering to the filter may usually be neglected if the same filter is employed for the next filtration of the oxalate. Heat the mixture in the beaker, and then dissolve the oxalates by the addition of as little hydrochloric acid as possible. Dilute to about 50 ml. with hot water, make alkaline with ammonia, and add about 1 ml. of the ammonium oxalate solution. Boil the mixture for about ten

minutes, allow to stand, hot, until settled, and then filter through the last filter. Wash well with hot water, to remove every trace of ammonium oxalate.

When little or no magnesium is present, one precipitation of calcium oxalate will be sufficient and will require only thorough washing with hot water.

e. To the 400-ml. beaker in which the oxalate precipitations were made, add 200 ml. of water and 10 ml. of sulfuric acid. Mix, heat to 70°C .³ drop in the filter paper and precipitate, and stir to effect the decomposition of the calcium oxalate, but avoid disintegrating the filter paper. Pull the paper up on the side of the beaker with the stirring rod and titrate the hot solution with standard potassium permanganate solution to the first permanent pink color. The potassium permanganate solution should be added very slowly at the start of the titration until the pink color, first formed, disappears rapidly. The addition of a pinch of manganous sulfate will speed up the reaction but is ordinarily unnecessary. Push the paper down into the solution and finish the titration.

Under the conditions named, the filter paper will exercise practically no influence on the result, and though the final pink tinge will gradually fade, there will be no difficulty in noting a sharp endpoint. Multiply the number of milliliters of permanganate required by the percentage value in CaO of 1 ml. to obtain the percentage of CaO in the ore.

For the preparation and standardization of the permanganate solution, see Chapter XXXIII.

D. Modifications

a. *Silicates and Substances Not Decomposed by Acids.* These are decomposed, as described under Silica, either by immediate fusion with alkali carbonate or by acid treatment, followed by fusion of the insoluble residue. The nature of the substance will determine these points precisely as with silica. When the solution eventually obtained contains considerable silicic acid, it is best to render it insoluble by evaporation and filter it off. A small amount of silicic acid may be neglected. The clear hydrochloric acid solu-

³ A critical study of the titration of oxalates by potassium permanganate solution is given in Research Paper 843 of the National Bureau of Standards.

tion finally obtained, containing all the calcium, is treated as described above (C, b or c).

b. *Fluorspar*. Place 0.5 gram of the material in a platinum dish with 3 grams of powdered potassium bisulfate and 5-6 ml. of sulfuric acid. Heat carefully, to avoid spattering, first to strong fumes, and then to a melt, if possible. If the mass solidifies at the end, without melting, cool sufficiently, add a little more sulfuric acid, and heat again. This will usually effect complete decomposition of the fluoride, even if the mass is not completely melted. Allow to cool, cover the dish, and dissolve the cake by warming with sufficient water, acidulated with 5 ml. of hydrochloric acid. Filter off any insoluble residue. Dilute to about 150 ml. with hot water, and proceed with the determination of CaO as described in C, b. Multiply the percentage of CaO found by 1.392 to obtain the percentage of CaF_2 .

c. *Phosphate Rock*. Most samples of phosphate rock decompose with nitric acid alone. If necessary, the insoluble material may be filtered off, ignited, fused with sodium carbonate, and combined with the main part of the solution after dehydration and removal of the silica. Carefully add dilute ammonia (sp. gr. 0.96) to the solution of the sample until a slight permanent precipitate forms. Heat to boiling, and add 10 ml. of a 10 per cent solution of oxalic acid. Stir until the iron and aluminum hydroxides are entirely dissolved and only a slight precipitate of calcium oxalate remains. Now add 200 ml. of boiling water and sufficient (20 ml.) saturated solution of ammonium oxalate to precipitate the calcium. Boil and stir for a few moments, remove from the heat, allow the precipitate to settle, and filter on an 11-cm. filter. Wash the precipitate and paper well with hot water. Transfer the precipitate back to the beaker, dissolve in hydrochloric acid, and repeat the precipitation. Filter through the same paper; continue as in C, e.

d. *Strontium and Barium*.⁴ Dry and ignite the oxalate precipitate obtained in C, d. Transfer the cooled oxides to a small Erlenmeyer flask, dissolve in nitric acid, and evaporate carefully to dryness at a temperature below 180°C . Powder the dry nitrates with a glass rod flattened on the end, and add 10 ml. of a mixture of equal parts of absolute alcohol and ether. Swirl, cork the flask,

⁴ R. Fresenius, *Z. anal. Chem.*, **32**, 189, 1893.

and allow to stand overnight. Filter on a small paper, and wash with the alcohol-ether mixture. Evaporate the filtrate to dryness, dissolve the residue in hydrochloric acid, and continue as in C, d.

e. *Small Amounts of Calcium.* If the calcium present is not in sufficient quantity to be conveniently titrated, the calcium oxalate precipitate may be dried, ignited over the blast lamp, and weighed directly as CaO.

II. RAPID VOLUMETRIC DETERMINATION

A. Application

The following rapid method for the determination of CaO is applicable to materials in which the calcium is present either as oxide, carbonate, or silicate, as in limestone, cement, lime, blast-furnace slags, etc. It is dependent on the fact that calcium can be completely precipitated as oxalate in solutions containing free oxalic acid, while iron, aluminum, and magnesium cannot.

B. Interfering Elements

In this method lead appears to interfere more or less, bringing the results high; it is therefore not so suitable for ores in general as the longer method first given.

C. Procedure

a. For high-grade *limestones*, that is, those which when burned do not give a hydraulic lime, weigh 0.5 gram into a platinum crucible, cover, and ignite for five minutes over a Bunsen burner, and then for five minutes over the blast lamp. This heating must be cautiously carried out, as magnesian stones are likely to fly out if heat is applied too suddenly. Start the ignition over a low Bunsen flame, gradually raise it until the full heat is attained, then continue for five minutes and follow with a blast lamp. Empty the contents of the crucible into a 500-ml. beaker and add 40 ml. of dilute (1 : 1) hydrochloric acid; heat, and when solution of the sample is complete proceed as in e.

b. For *cement rock* or *hydraulic limestones*, weigh the sample as before and carefully mix with it $\frac{1}{4}$ gram of finely ground sodium carbonate, by stirring with a glass rod. Brush off the rod into the crucible and ignite over a Bunsen burner, starting with a low flame

and gradually raising it until the full heat is attained. Continue heating for five minutes longer, and then ignite over the blast for the same length of time. Place the crucible in a 500-ml. beaker, and decompose the sintered mass in the crucible with 40 ml. of dilute (1 : 4) hydrochloric acid, keeping the beaker covered to avoid loss by effervescence. Heat until solution is complete, and proceed as in e.

c. For *cement*, pass the sample through a 100-mesh screen, weigh 0.5 gram into a dry 500-ml. beaker, and add, with constant stirring, 20 ml. of water. Break up the lumps, and, when all the sample is in suspension except the heavier particles, add 20 ml. of dilute (1 : 1) hydrochloric acid and heat until solution is complete. This usually takes five or ten minutes. Proceed as in e.

d. Many *slags* are soluble in concentrated hydrochloric acid. In dealing with such material, weigh 0.5 gram into a 500-ml. beaker, stir up with a very little water, add 20 ml. of strong hydrochloric acid, and heat. When solution is complete, proceed as in e.

e. Carefully add dilute ammonia to the solution of the sample (from a, b, c, or d) until a slight permanent precipitate forms. Heat to boiling, and add 10 ml. of a 10 per cent solution of oxalic acid. Stir until the iron and aluminum hydroxides are entirely dissolved and only a slight precipitate of calcium oxalate remains. Now add 200 ml. of boiling water and sufficient (20 ml.) saturated solution of ammonium oxalate to precipitate the calcium. Boil and stir for a few minutes, remove from the heat, allow the precipitate to settle, and filter on an 11-cm. filter. Wash the precipitate and paper well with hot water. Remove the filter from the funnel; open, and lay against the sides of the beaker in which the precipitation was made; wash from the paper into the beaker with hot water; add 200 ml. of water and 10 ml. of sulfuric acid; and fold the paper over and allow to remain against the walls of the beaker. Heat to 70° C. and titrate with standard potassium permanganate until a pink color is obtained; now drop in the filter paper, stir until the color is discharged, and finish the titration carefully, drop by drop.

CHLORIDE MINERALS

Mineral Name	Chemical Formula	% Cl	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Halite.....	NaCl	60.6	White to pink	2.2	Ca, Mg, Fe, Si, K	Water soluble	
Sylvite.....	KCl	47.6	White to pink	2.0	Ca, Mg, Fe, Si, Na	Water soluble	
Carnallite.....	KCl·MgCl ₂ ·6H ₂ O	38.3	White to pink	1.6	Ca, Fe, Si, Na	Water soluble	
Cerargyrite.....	AgCl	24.7	White, shiny luster, tar- nishes brown	5.5	Pb, Cu, Zn, Hg, Fe, S	H ₂ SO ₄ + Zn	Na ₂ CO ₃
Atacamite.....	CuCl ₂ ·3Cu(OH) ₂	16.6	Yellowish green	3.8	CO ₂ , S, Fe, Si	HNO ₃ , H ₂ SO ₄	
Pyromorphite.....	3 Pb ₃ P ₂ O ₈ ·PbCl ₂	2.6	White to yellowish	6.5	As, S, CO ₂ , Ca	HNO ₃	
Vanadinite.....	3 Pb ₃ V ₂ O ₈ ·PbCl ₂	2.5	White to yellowish	6.7	As, P, Mo, Zn, Cu	HNO ₃	
Chlorapatite.....	3 Ca ₃ (PO ₄) ₂ ·CaCl ₂	6.8	White or tinted	3.2	Si, Fe, Mn, Ti, Mg, Na, K	HNO ₃	Na ₂ CO ₃

Chlorine is present in small amounts in gangue minerals of high soda content, such as sodalite or wernerite. These minerals are partly broken up by nitric acid and yield readily to alkaline fusion.

CHAPTER X

CHLORINE

I. GRAVIMETRIC METHOD

A. Application

This method serves well for practically all types and grades of ores and ore products. Ordinarily a simple separation of the insoluble material is all that is necessary before precipitation of the silver chloride.

B. Interfering Elements

Of the elements forming precipitates with silver nitrate in weak acid solution, arsenic, phosphorus, chromium, vanadium, molybdenum, and tungsten are occasionally encountered. These compounds are much more soluble in nitric acid than the chloride, and do not interfere in ordinary analyses if present in moderate amounts. Bromides and iodides interfere, but are not encountered in ore analysis.

C. Procedure

a. Treat 0.25 to 5 grams of the ore with 5 per cent nitric acid. Warm until any sulfides present are decomposed, but avoid overheating. Neutralize the solution, and add an excess of ammonium hydroxide. Heat to boiling, and filter. Wash the precipitate of hydroxides and insoluble material back into the beaker and dissolve in dilute sulfuric acid. Examine the insoluble residue.

b. If insoluble chlorides are believed to be present, the residue may be decomposed by fusion with sodium carbonate. Leach the melt with hot water, acidify the extract carefully with nitric acid, and boil off the carbon dioxide. Make alkaline with ammonium hydroxide, boil, and filter off any precipitate. Combine the filtrate with that obtained from the original acid treatment.

c. Neutralize the ammonia solution with nitric acid and add 1 ml. in excess for each 100 ml. of solution. Precipitate the chloride

with 5 per cent silver nitrate solution in slight excess. Warm the solution on the steam plate until the precipitate of silver chloride coagulates and settles. Add a little paper pulp and filter on a close paper, washing with a 1 per cent nitric acid solution. Transfer the precipitate and pulp back to the beaker and dissolve with warm dilute ammonium hydroxide. Filter off the paper pulp on the same paper and wash well with 2 per cent ammonia wash solution. Acidify the filtrate with nitric acid and reprecipitate the silver chloride as before. Allow to set on the steam plate, stirring occasionally, until the precipitate coagulates well. Filter on a tared Gooch crucible, dry at 105° C., and weigh as silver chloride. Multiply the weight of AgCl by 0.2474 to obtain the weight of chlorine.

D. Modifications

Cerargyrite is not decomposed by dilute nitric acid treatment, but is readily broken up by treatment with warm dilute sulfuric acid and granulated zinc metal. The silver is reduced to the metal, and the chloride ion is retained in solution. The acid solution should be heated only enough to cause a rapid generation of hydrogen, as chlorine may be lost by volatilization in hot solution. Copper, lead, bismuth, mercury, tin, cadmium, etc., are reduced to the metallic state along with the silver. More or less of the arsenic and antimony will be lost as arsine and stibine.

II. MOHR'S¹ VOLUMETRIC METHOD

A. Application

The following method is best applied to water-soluble chlorides and solutions.

B. Interfering Elements

Elements such as lead and barium that form insoluble chromates consume the indicator solution. Mercury, lead, thallium, and copper that form insoluble chlorides may cause trouble.

C. Procedure

a. The chloride solution should be cold and neutral. If acid, it should be neutralized with pure sodium or calcium carbonate in slight excess. To the cold neutral, or faintly alkaline, solution con-

¹ C. F. Mohr, *Liebig's Ann.*, 97, 335, 1856.

tained in a porcelain casserole or evaporating dish add 1 ml. of a 2 per cent solution of neutral potassium chromate.² Titrate with a 0.1 *N* solution of silver nitrate until a permanent faint red tinge is obtained, due to the formation of silver chromate. This compound cannot exist permanently in the mixture until all the chlorine has been precipitated as silver chloride. The mixture should be well stirred after each addition of silver nitrate, which toward the last should be added drop by drop. As the faint reddish tinge is somewhat difficult to distinguish, various schemes have been proposed to facilitate its detection. The authors have found it a good plan, when the end point is apparently attained, after the buret is read, to pour off half the liquid into a similar casserole and then add 1 more drop of the silver nitrate solution to one casserole and note whether the two portions of the liquid then show any difference. When such a difference can be detected, the end point has certainly been reached, and it is usually safe to accept the reading of the buret taken previous to the last drop. For accurate work a blank test should be made on the same volume of liquid to see how much silver solution is required to produce a tint when no chloride is present, and this amount must be deducted from that used in the analysis. Multiply the number of milliliters used by 0.003546 to obtain the weight of the chlorine present, or by 0.005845 for the weight of the corresponding sodium chloride.

See **Chapter XXXIII** for the preparation of 0.1 *N* silver nitrate.

III. VOLHARD'S³ VOLUMETRIC METHOD

A. Application and Interfering Elements

Same as for Procedure I.

B. Procedure

Obtain a nitric acid solution of the chlorides as in Procedure I, C, a, b, and c. Run in the silver solution from a buret until sure of a light excess, and then boil the mixture until the silver chloride

² Adsorption indicators such as fluorescein, dichlor (R) fluorescein, eosin, bromphenol blue, and rhodamine 6 G, have been recommended by Fajans, Kolthoff, Böttger, and others. (See Brennecke-Fajans-Furman-Lang-Stamm, *Newer Methods of Volumetric Chemical Analysis*, translated from the German edition by R. E. Oesper, D. Van Nostrand Co., Inc., 1938.)

³ J. Volhard, *Liebig's Ann.*, 190, 1, 1878.

settles well on short standing.⁴ Cool completely, add a few milliliters of the ferric indicator, and titrate with the thiocyanate solution to a faint brownish tint. Note the amount of thiocyanate used, calculate its value in silver solution, and deduct this from the amount of silver solution used. The remaining silver solution is the amount required to form silver chloride with the chlorine in the salt or liquid taken, and from this all necessary calculations can be made, as in Procedure II.

For the preparation and standardization of the solutions, see Chapter XXXIII.

The indicator solution consists of a saturated solution of ferric ammonium sulfate with sufficient nitric acid added to remove most of the brown color.

⁴ Precipitated AgCl does not interfere with the thiocyanate titration if it has been well coagulated by boiling. If allowed to remain in an opalescent or cloudy condition it will quickly decompose the slight excess of thiocyanate that causes the end-reaction color. The color will disappear repeatedly as more thiocyanate is added and will prevent a correct determination of the end point. This is because silver thiocyanate is more insoluble than silver chloride.

CHROMIUM MINERALS

Mineral Name	Chemical Formula	% Cr ₂ O ₃	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Chromite.....	FeO·Cr ₂ O ₃	68.0	Brown to brownish black	4.5	Mg, Al, Ca, Mn, Si	H ₃ PO ₄ + H ₂ SO ₄ + HClO ₄	Na ₂ O ₂
Picotite.....	(Fe,Mg)O·(Al,Cr) ₂ O ₃	Variable 40-55	Brown to greenish brown	4.1	Ca, Mn, Si, CO ₂	Same	Same
Crocoite.....	PbCrO ₄	31.1	Orange-yellow	6.0	Cu, P, S	HNO ₃ , HClO ₄	

Chromium occurs in small amounts in a number of gangue minerals of high magnesium content, such as serpentine, diopside, talc, enstatite, and olivine. These minerals are usually greenish to greenish brown in color. Chromium ores are characterized by their resistance to decomposition.

CHAPTER XI

CHROMIUM

I. VOLUMETRIC METHOD

A. Application

The following procedure is applicable to iron and chromium ores, rocks, minerals, steel, and metallurgical products, containing chromium in sufficient amount to be titrated.

B. Interfering Elements

Of the elements present with chromium in the extract from a peroxide fusion, none offer any interference unless in unusual amounts such as to mask the end point of the titration.

C. Procedure

a. Grind the ore in an agate mortar to the finest possible powder. Weigh 0.5 gram into a spun-iron crucible of about 20 to 25-ml. capacity. Add about 5 grams of sodium peroxide, mixing thoroughly with a glass rod. Good sodium peroxide is of a yellowish color. Reject any that is white, as it has become decomposed. Holding the crucible with tongs, heat over a Bunsen burner.

The operation requires careful watching. Only a low red heat is necessary, but, as the mass is slow in fusing, one is apt to heat the bottom of the crucible to bright redness. When this happens the peroxide is likely to attack the crucible and perforate it. If care is taken, and the crucible is tipped from side to side, the mass gradually softens and becomes liquid around the sides.

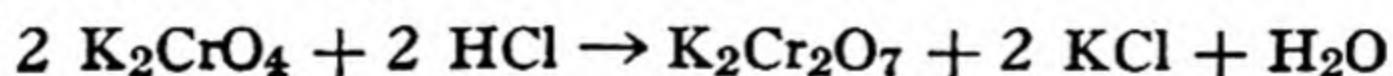
Now give the crucible a rotary motion, never allowing the temperature to become much higher than a low red heat, until all unfused material, floating in the center, has liquefied like the rest. When the rotary and tipping movements have been continued for several minutes more, the operation may be considered finished. If manipulated as described, the same crucible should serve for many fusions; otherwise the crucible and analysis may easily be ruined.

Have ready a 4-inch porcelain casserole containing about $\frac{3}{4}$ inch of cold water, or somewhat less than the height of the crucible. Set the partly cooled crucible carefully in this, avoiding the entrance of any water. Cover the casserole, and, as soon as apparently safe, insert a glass rod under the cover and upset the crucible. The contents will quickly boil out and disintegrate without any further heating. When the action is over, remove and rinse the cover, lift out the crucible on the rod, and wash the outside with cold water. Now, holding the crucible with the fingers, similarly rinse out the inside. Again replacing the cover, heat the mixture to boiling and then boil gently for exactly ten minutes. This is to make certain that all the peroxide present is decomposed. If the volume of liquid gets low, add hot water. Remove from the heat, dilute somewhat with cold water; then lift the edge of the cover, and quickly add about 5 grams of ammonium carbonate. The dilution and cooling are to lessen any possible effervescence. The ammonium carbonate neutralizes a portion of the sodium hydroxide and renders the solution less likely to destroy a filter. It must not be added, however, until the sodium peroxide has been decomposed by boiling, as otherwise some ammonium nitrite would be formed that would subsequently cause a high result. As soon as the ammonium carbonate has dissolved, the mixture is ready for filtration. The filtration is best done through asbestos¹ with suction, four or five washings usually being sufficient.

b. The filtrate now contains the chromium as sodium chromate. Transfer it to a flask of about a liter capacity and cool under the tap. Have ready some cold 1 : 1 hydrochloric acid. Pour this into the chromium solution very cautiously (on account of effervescence) until the solution is plainly acid. This is usually shown by the change of color from yellow to orange.² If the color change is not apparent, litmus paper may be used, but not left in the solution. Now add about 25 ml. more of the same 1 : 1 acid, dilute if necessary to 300-400 ml., and see that the solution is perfectly cold. It is now ready for the titration.

¹ Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 409, John Wiley & Sons Inc., 1929.

² Neutral chromate is changed to dichromate:



c. If potassium iodide is now added, the chromic acid present will liberate iodine,³ which is then titrated with a standard solution of sodium thiosulfate.⁴ Allow about 1 gram of potassium iodide for every 20 per cent of chromium possibly present. Never use less than 1 gram. More may be added at the end of a titration, as a test, and the titration continued on any additional iodine set free, without vitiating the final result. It is convenient to employ a 50 per cent solution of potassium iodide with a short 2-ml. pipet in the bottle. After adding the potassium iodide, titrate at once with the standard thiosulfate until the brown color of the iodine has become faint. Now add a few milliliters of starch solution (**Chapter XXXIII**), and continue the titration cautiously, until a single drop completely discharges the last trace of color produced by the starch and leaves the solution a clear, pale green or bluish green tint if much chromium is present. The end point is very sharp, and without care is very easily passed. Multiply the number of milliliters of thiosulfate used by the percentage value for chromium of 1 ml. to obtain the result.

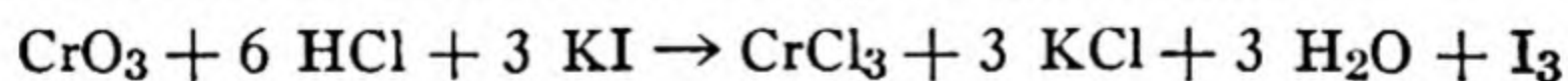
If the end point should be passed, add potassium permanganate of any strength, drop by drop, from a buret, counting the drops, until the blue color is restored. Again finish the titration and note the buret reading; then add the same number of drops of permanganate as before, and once more finish with the thiosulfate, and note reading. Deduct this additional amount of thiosulfate from the previous reading to obtain the true reading for chromium.

See **Chapter XXXIII** for the preparation and standardization of the thiosulfate solution.

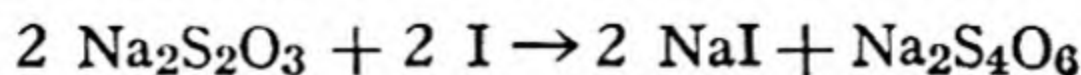
D. Modifications

a. *Permanganate-Ferrous Ammonium Sulfate Method.* Treat the sample as above as far as C, b. Acidify the filtrate with dilute sulfuric acid (1 : 4), and then add 25 ml. or more in excess. If the solution has a pinkish tinge due to the presence of manganese in

³ The reaction between chromic acid and potassium iodide is



⁴ The reaction between sodium thiosulfate and iodide is:



Sodium iodide and tetrathionate are formed.

its highest valence, add 1 to 2 ml. of dilute hydrochloric acid to reduce it. After allowing the solution to cool, transfer it to a large beaker and dilute to 700 ml. with cold water.

The chromium in the solution now exists as chromic acid. Add a measured amount of ferrous ammonium sulfate solution in excess of that necessary to reduce the chromic acid, and titrate the excess with standard potassium permanganate solution. Determine the volume of permanganate equivalent to 1 ml. of the ferrous ammonium sulfate solution and again titrate to an end point with the permanganate solution. Calculate the amount of permanganate solution equivalent to the total ferrous ammonium sulfate solution used and deduct the amount of permanganate used in titrating. Multiply the result by the chromium factor for the permanganate solution to obtain the percentage of chromium. The percentage of chromium multiplied by 1.4614 equals the percentage of Cr_2O_3 . The preparation and standardization of the solution are described in Chapter XXXIII.

b. *Perchloric Acid Method.* Smith and Getz⁵ recommend an acid decomposition for chromite using sulfuric, phosphoric, and perchloric acids. The decomposition is accomplished by digestion with 10 ml. of a mixture of 8 parts of 95 per cent sulfuric acid and 3 parts of 85 per cent phosphoric acid. The decomposed sample is cooled and the chromium oxidized by digestion at 215° C. with 12 ml. of a solution of 2 parts 72 per cent perchloric acid to 1 part of water. The weight of chromite taken should not exceed 150 mg.

II. GRAVIMETRIC METHOD

A. Application

The following method is applicable to small amounts of chromium to be determined in the course of a general analysis.

B. Interfering Elements

No elements interfere if present in moderate amounts. Zinc, in excessive amounts, will be only partially removed by a single precipitation with ammonium hydroxide and may be later precipitated as chromite.

⁵ G. Frederick Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, 9, 518, 1937.

C. Procedure

Fuse 1 gram of the very finely ground ore with a mixture of 5 grams of sodium carbonate and 0.5 gram of potassium nitrate in a platinum crucible or small dish. After fusion, extract the melt with hot water and transfer the mixture to a small beaker. If the solution is colored by manganese, add a little alcohol and warm the mixture. This will precipitate the manganese as dioxide. Allow the precipitate to settle, and note the color of the clear solution. If chromium is present it will be more or less yellow. If quite colorless, chromium may be considered absent. Filter the mixture, washing with water, and dry and ignite the insoluble residue and the filter. Now grind it with ten times its weight of sodium carbonate and a little potassium nitrate; fuse the mixture, and extract with water, etc., as before. Filter and add the filtrate to the former one. Acidify the combined filtrates with hydrochloric acid, and evaporate to dryness to render the silica insoluble and reduce the chromic acid to Cr_2O_3 . Take up in hydrochloric acid, dilute, and filter. Precipitate the Cr_2O_3 and Al_2O_3 in the filtrate with ammonia. Boil for a short time, filter, and wash well with hot water. Dry and ignite the precipitate, and then fuse it with as little sodium carbonate and potassium nitrate as possible. Extract the melt with water, and transfer the mixture to a platinum dish. Evaporate the liquid until it is very concentrated, adding crystals of ammonium nitrate from time to time to change all the carbonated and caustic alkali to nitrate. Each addition of the ammonium nitrate produces an effervescence and ammonium carbonate is given off. The solution finally becomes almost syrupy and smells faintly of ammonia, the addition of ammonium nitrate no longer causing an effervescence. Now add a few drops of ammonia, and filter from the precipitated alumina, aluminum phosphate, manganese dioxide, etc. The filtrate contains the chromium as alkali chromate. Add an excess of a strong solution of sulfur dioxide, which changes the color of the solution from yellow to green. Boil well, add an excess of ammonia, boil again for a few minutes, filter on an ashless filter, and wash thoroughly with hot water. Dry and ignite the precipitate, and weigh as Cr_2O_3 . Multiply the weight by 0.6842 to obtain that of the chromium.

III. COLORIMETRIC METHOD ⁶

A. Application

Minute amounts of chromium are best determined by a colorimetric method. The following procedure, though not new, is rapid and convenient for the ordinary technical analysis of materials such as bauxite and clays.

B. Procedure

Place the alkaline chromate solution, obtained by fusion with sodium peroxide or sodium carbonate and niter and extraction with water, in a colorimetric tube, and dilute to the mark. If the yellow color is deeper than that of the standard solution, an aliquot part should be used. Place a definite amount of distilled water containing a little sodium carbonate or sodium hydroxide in a corresponding colorimetric tube, and add the standard potassium dichromate solution (Chapter XXXIII) slowly from a buret, with stirring, until the color matches that of the unknown. Calculate the percentage of chromium or Cr_2O_3 from the number of milliliters of dichromate used.

⁶ W. F. Hillebrand, *J. Am. Chem. Soc.*, 20, 454, 1898.

COBALT MINERALS

Mineral Name	Chemical Formula	% Co	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Smaltite-chloanthite . .	(CoNi)As ₂	Variable	Grayish black, metallic luster	5.7 to 6.8	Fe, S, Ag, Bi, Cu, Pb, Zn	HNO ₃	KHSO ₄ , Na ₂ CO ₃
Cobaltite	CoS ₂ ·CoAs ₂	35.5	Same	6.3	Fe, Ni, Ag, Cu, Mo	HNO ₃	Same
Linnaeite	CoS·Co ₂ S ₃	57.9	Same	5.0	Ni, Fe, Cu, Pb, Zn	HNO ₃	Same
Erythrite	3CoO·As ₂ O ₅ ·8H ₂ O	29.5	Pale crimson to orange- red	3.0	Ni, Fe, Cu, Pb, Zn, Ca, Mg	HCl	Same

Most cobalt minerals yield readily to an attack by acids, giving pink to red solutions. In the absence of water, concentrated hydrochloric acid produces a deep blue color. Cobalt is found most commonly combined with nickel, iron, copper, arsenic, and sulfur; and occasionally with calcium, magnesium, bismuth, or antimony.

CHAPTER XII

COBALT

I. NITROSO-BETA-NAPHTHOL METHOD ¹

A. Application

The method is especially suitable for the determination of cobalt in the presence of comparatively large amounts of nickel. Nitroso-beta-naphthol, $C_{10}H_6O(NO)$, forms with cobalt the compound $Co[C_{10}H_6O(NO)]_3$, cobalti-nitroso-beta-naphthol, which is insoluble in hydrochloric acid, the corresponding nickel compound being soluble. Like most organic reagents for the metals, nitroso-beta-naphthol produces a very voluminous precipitate with cobalt, inhibiting precipitations of more than 100 mg. of the metal, owing to the inconveniences encountered in the manipulation. The method, therefore, is most easily applied to medium- or low-grade materials.

B. Interfering Elements

None of the ordinary elements interfere with the method as described. For a detailed description of the behavior of the elements in precipitations with zinc oxide and nitroso-beta-naphthol, see the National Bureau of Standards, *Journal of Research*, vol. 7, 883, 1931; and Lundell and Hoffman's *Outlines of Methods of Chemical Analysis*, John Wiley & Sons, Inc., 1938.

C. Procedure

a. Weigh an appropriate amount of the material containing not more than 0.2 gram of cobalt. Decompose the sample by treatment with nitric and hydrochloric acids. Examine the insoluble material, and, if not properly decomposed, dilute the mixture with about 50 ml. of water, warm, and filter. Dry, and ignite the residue, and fuse it with 5 grams of potassium bisulfate in a silica crucible.

¹ M. Ilinsky and G. v. Knorre, *Ber.*, 18, 669, 1885.

Dissolve the melt in the original filtrate, and take the solution to dryness on the hot plate. Most samples are broken up by acid treatment alone and may be taken directly to dryness. Cool, take up the residue in 5 ml. hydrochloric acid and 100 ml. of water, heat until all soluble salts are in solution, and filter off the insoluble.

b. Pass hydrogen sulfide gas into the warm filtrate until all the members of the acid H_2S group are precipitated. Allow the precipitate to coagulate and settle. Filter off the sulfides, washing with hydrogen sulfide water, and receiving the filtrate in a 400-ml. beaker. Boil the filtrate until the hydrogen sulfide is expelled, then add a little bromine water to oxidize the iron, and boil off the excess.

c. Transfer the oxidized solution to a 500-ml. volumetric flask and dilute to about 300 ml. Add an emulsion of carbonate-free zinc oxide slowly, while swirling the flask, until all the iron is precipitated and the zinc oxide is in evident excess as shown by the presence of undissolved zinc white. Dilute to the mark with hot water, and allow to stand until the precipitate has settled well. The amount of cobalt present may be estimated at this point by the pink color of the solution. Decant the supernatant liquid from the flask through a close filter paper, and, to exactly 250 ml. of the filtrate (representing one-half of the original weight of sample) in a 600-ml. beaker, add 6 ml. of hydrochloric acid, dilute to 300 ml., and heat to boiling.

d. Now, for every 1 per cent of cobalt presumed to be present, add 4 ml. of a freshly prepared solution of nitroso-beta-naphthol. This solution is made by dissolving 1 gram of the salt in 10 ml. of glacial acetic acid. After adding the reagent, boil for about two minutes, then remove from the heat, stir well, and set aside for a short time until the bright red precipitate settles.

Filter the hot solution through a filter of convenient size. Rinse out the beaker with hot 1 : 1 hydrochloric acid, then wash the filter and precipitate five times with this acid, alternating with five washes with hot water. Finally wash ten times with hot water.

Transfer filter and precipitate to a weighed quartz or porcelain crucible, ignite gently until the carbonaceous matter is burned off, and then to constant weight at a temperature of 800 to 900° C.

Weigh the residue as Co_3O_4 . This weight, multiplied by 0.7342, will give the weight of the cobalt.

If desired, the Co_3O_4 may be reduced in hydrogen and weighed as metal.

II. ELECTROLYTIC METHOD

A. Application

The following procedure is best applied to nickel and cobalt ores and products containing from moderate to large amounts of cobalt. Like most electrolytic methods, the electrolysis must be performed in relatively pure solutions, thereby necessitating preliminary separations of most of the metals.

B. Interfering Elements

The most common interfering element is zinc, which is best separated by precipitation with hydrogen sulfide in 0.01 *N* sulfuric acid solution. Vanadium, tungsten, chromium, and molybdenum present in excess of the amount held by the iron in the basic acetate separation will contaminate the cobalt and nickel.

C. Procedure

a. Treat 1 gram of the ore in a 250-ml. beaker with 10 ml. of strong nitric acid and 5 ml. of strong hydrochloric acid. When decomposition is complete add 10 ml. of strong sulfuric acid and boil until the sulfuric acid is fuming strongly. Allow to cool, take up with water, add 5 ml. of strong hydrochloric acid to assist solution, and boil gently for a few minutes.

b. Remove from the heat and pass hydrogen sulfide through the hot solution for ten to fifteen minutes, then heat again and once more pass in hydrogen sulfide until all the arsenic is precipitated and the supernatant liquid is clear. Filter, washing the precipitate six or seven times with hot water. Boil the filtrate to expel the hydrogen sulfide, and reduce to a volume of about 150 ml. Filter and wash as before. Heat the filtrate to boiling, and add 15 to 20 ml. of hydrogen peroxide to effect oxidation.

c. After boiling a short time, remove from the heat and allow to cool somewhat, and then separate the iron as basic acetate as follows: Make the solution just alkaline with ammonia and then reacidify slightly with hydrochloric acid. Add 15 grams of solid sodium acetate (crystals), and boil. Filter off the iron precipitate,

washing with hot water, and place the filtrate over the heat to concentrate. Dissolve the precipitate in hot dilute hydrochloric acid, dilute to about 150 ml., and repeat the precipitation as just described. Unite the two filtrates, boil down to about 100 ml., and filter. Make the filtrate alkaline with ammonia, adding about 20 ml. in excess.

d. Electrolyze the hot solution (which should have a volume of 125 to 130 ml.), keeping it hot and highly ammoniacal during the electrolysis. A gauze cathode is preferred, with a current density of $ND_{100} = 0.5-0.7$ ampere and an electrode tension of 2.8-3.3 volts. When the operation is apparently finished (in $2\frac{1}{2}$ to $3\frac{1}{2}$ hours), test for nickel and cobalt with sodium sulfide paper. Wash the cathode first with water, then with alcohol, dry at about 100°C ., and weigh. This gives the combined nickel and cobalt.

Dissolve the deposit in a 250-ml. beaker in strong nitric acid, and wash off the cathode with hot water. Boil or evaporate the solution to a syrup. Add about 20 ml. of water, and then add a solution of potassium hydroxide until a precipitate of cobalt hydroxide (blue) remains undissolved. Now acidify with acetic acid and add a few milliliters in excess; then add about 25 grams of potassium nitrite and stir until dissolved. Boil gently for about twenty minutes, then dilute with water until the beaker is about five-sixths full; allow to stand overnight. Decant and filter the cobalt precipitate and wash it a few times with ice-cold water, or water containing about 5 per cent of potassium nitrite and barely acidified with acetic acid. Dissolve the precipitate in hot dilute sulfuric acid, and boil down the solution until the sulfuric acid is fuming. Cool, dilute with water, heat to boiling, and filter. Make the filtrate alkaline with ammonia, having about 20 ml. in excess, dilute to about 125 ml. and electrolyze as described above. Wash the cathode first with water, then with alcohol, dry at about 100°C ., and weigh as cobalt. The nickel may be determined by the difference between this weight and that of the combined nickel and cobalt.

D. Modification

As an alternate method, the deposit of cobalt and nickel (C, d) may be dissolved in nitric acid, evaporated to a small volume, an excess of hydrochloric acid added, and the solution evaporated to

dryness to expel the nitric acid. Take up the residue in 5 ml. hydrochloric acid, transfer to a 100-ml. volumetric flask, and dilute to the mark. Pipet an appropriate aliquot part into a 600-ml. beaker, add enough hydrochloric acid to make a total of 6 ml. in all, dilute to 300 ml., heat to boiling, and precipitate the cobalt as described in Procedure I, C, d.

COPPER MINERALS

Mineral Name	Chemical Formula	% Cu	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Chalcopyrite.....	CuFeS ₂	34.5	Greenish black	4.2	Commonly associated with Au, Ag, Pb, Zn, Cd, Bi, As, Sb, Sn, Fe, Co, Ni, and Mn. Occasionally with Hg, Se, Te, Mo, Tl, W, U, and V	HNO ₃	
Bornite.....	Cu ₅ FeS ₄	63.3	Grayish black	5.0		HNO ₃	
Cuprite.....	Cu ₂ O	88.8	Brownish red, shining	6.0		HNO ₃ , HCl	
Tenorite.....	CuO	79.8	Black, earthy	6.5		HNO ₃ , HCl	
Chalcocite.....	Cu ₂ S	79.8	Lead-gray	5.8		HNO ₃	
Covellite.....	CuS	66.4	Black, shining	4.6		HNO ₃	
Tetrahedrite.....	5Cu ₂ S·2(Cu,Fe,Zn)S·2Sb ₂ S ₃	Variable	Gray to black, reddish or brownish	5.1		Aqua regia	
Tenanthite.....	5Cu ₂ S·2(Cu,Fe,Zn)S·2As ₂ S ₃	Variable	Gray to black, reddish or brownish	4.5		Aqua regia	
Malachite.....	CuCO ₃ ·Cu(OH) ₂	57.5	Pale to bright green	4.0		HNO ₃ , HCl	
Azurite.....	2CuCO ₃ ·Cu(OH) ₂	55.4	Blue	3.9		HNO ₃ , HCl	
Atacamite.....	CuCl ₂ ·3Cu(OH) ₂	14.9	Apple-green	3.8		HNO ₃ , HCl	
Chrysocolla.....	CuO·SiO ₂ ·2H ₂ O	36.2	Bluish green to white	2.2		HNO ₃	
Enargite.....	3Cu ₂ S·As ₂ S ₅	48.3	Gray to black, sooty	4.4		Aqua regia	
Native copper.....	Cu	±95	Copper color, metallic	8.8		HNO ₃	

Copper occurs in varying amounts in a great many types of ore deposits. No difficulty is encountered in obtaining copper in solution, and its presence is readily detected by the green or blue colors of its salts.

CHAPTER XIII

COPPER

I. VOLUMETRIC IODIDE METHOD

A. Application

The iodide method is one of the most accurate methods known for the determination of copper, and possesses the advantage of being applicable to complex ores, as few elements offer any interference.

B. Interfering Elements

None of the common elements interfere if the procedure is carefully followed. Lead and bismuth are without effect, except that by forming colored iodides they may mask the approach of the end point before the starch solution is added. Arsenic and antimony must be in their higher valences, and, under the treatment described, they have no influence.

C. Procedure

a. To 0.5 gram of the ore in an 8-oz. flask add 10 ml. of strong hydrochloric acid and 5 ml. of strong nitric acid. Boil until decomposition is complete, using more of the acids if necessary (and enough at the end to hold all soluble salts in solution), and then add 8 ml. of strong sulfuric acid and boil to abundant fumes, best over a free flame, but do not boil off much of the sulfuric acid.¹

After cooling, boil with about 30 ml. of water for a moment and then allow to stand, hot, until any anhydrous ferric sulfate has entirely dissolved; then filter through a 9-cm. filter to remove more especially any lead sulfate. Receive the filtrate in a beaker about 6 cm. in diameter. Wash the filter and residue at least six times with hot water. The final volume of the filtrate will ordinarily not

¹ If impure sulfur separates, it is best cleaned by allowing the strong sulfuric acid to continue just at a boil (so as not to evaporate much) for some time.

much exceed 75 ml. Place in the beaker a piece of stout sheet copper-free aluminum about an inch and a half square and with the alternate corners bent in opposite directions for about a quarter of an inch, so as to prevent the plate from lying flat on the bottom. (The same aluminum may be used repeatedly as it is but little attacked each time.)

b. Cover the beaker and heat to boiling. After boiling about ten minutes all the copper (also Au, Ag, Pt, Hg, Sn, Bi, Cd, Se, Te, Co, Ni, and Tl) should be precipitated, if the volume of the solution did not much exceed 75 ml. As a test, inject a little hydrogen sulfide water from a wash bottle through the lip of the beaker. If more than a faint brown color is produced, boil longer, until the solution clears by coagulation of the precipitate, and again test. Do not boil to a very small bulk, as some of the precipitated copper might then redissolve. Add water, if necessary, to prevent this. The hydrogen sulfide test will finally become negative or show only a faint brownish tinge. Now remove from the heat and wash down the cover and sides of the beaker with hydrogen sulfide water. This will prevent any of the finely divided copper from becoming oxidized and dissolved and will also precipitate any traces of copper that may still remain in solution. (It should be understood that there is never any difficulty in precipitating *all* the copper as metal.)

Decant through a 9-cm. filter (using a loop funnel by preference), and then, without delay, rinse the copper into the filter with a jet of hydrogen sulfide water, leaving the aluminum, as clean as possible, in the beaker. Traces of adhering copper will be recovered later. Wash filter and precipitate six times with hydrogen sulfide water. Allow to drain completely each time; but never permit the filter to remain drained a single moment, until the washing is finished, or copper may oxidize and run through.

c. Now place the original clean flask under the funnel, then open the filter carefully and spread it smoothly in the funnel, against one side. With a jet of hot water, using as little as possible, wash the precipitate into the flask. If it is apparently too bulky to pass easily through the funnel, proceed as follows: Support the paper, scoop-shaped, in the hand, over the flask, and wash in the main portion of the precipitate, then replace it in the funnel, with the flask underneath, and wash in the remainder.

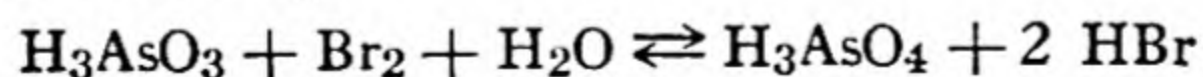
Pour 5 ml. of strong nitric acid over the aluminum in the beaker, shake it about so as to dissolve any adhering copper, and then pour from the beaker over the filter, still retaining the aluminum in the beaker. Without washing beaker or filter at this stage, collect the filter into a small compass with a glass rod, and push it gently, with moderate compactness, into the apex of the funnel. Level the top of the mass, but avoid compressing so tightly as greatly to impede filtration. Next, remove the flask and replace it with the beaker.

Boil the mixture in the flask to dissolve the copper and expel the red fumes. If the liquid is too dilute, so that the copper fails to dissolve immediately, continue boiling until solution of everything is complete, including any copper sulfide present. Finally, again place the flask under the funnel. Now pour over the filter 5 ml. or more of saturated bromine water, or enough to impart a distinct color to the liquid in the flask. The bromine cleanses any residue still adhering to the filter, but its most important function is to insure the highest state of oxidation of any arsenic or antimony in the solution.² Now wash the beaker and aluminum with hot water, pouring through the filter, then wash the filter six times. The final volume in the flask need not much exceed 50-60 ml.

Boil the solution until the excess of bromine is entirely expelled and the volume is reduced to perhaps 25 ml. Cautiously add a small excess of ammonia to the boiling liquid, allowing it to run slowly down the side of the flask (usually 10 ml. or a little more). Boil off most of the excess, that is, until the odor is faint. Now add 5 ml. of glacial acetic acid and boil for about a minute more. This last boiling is very important, as it tends to remove the last traces of oxidizing compounds that might cause a return of the blue color at the end of the titration. Cool completely under the tap.

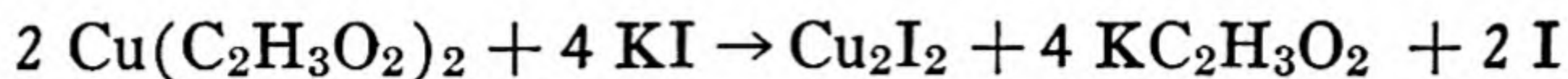
d. Dilute to about 30 ml. if necessary, add potassium iodide in the proportion of 2 ml. of a 50 per cent solution for every 15 per

² The reaction, in case any *ous* compounds of arsenic or antimony are present, is in accordance with the following:



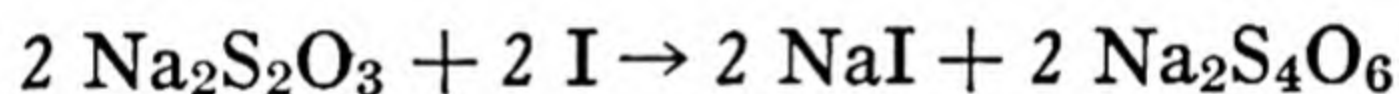
This reaction is reversible, but, under the conditions prevailing, proceeds as shown. It is easily realized that, if bromine is not thus allowed to convert the *ous* to *ic* compounds, the liberated iodine will do it later, and any iodine thus consumed will cause a correspondingly low copper result.

cent copper assumed to be present, but never less than 2 ml. Cuprous iodide will be precipitated and iodine liberated according to the reaction:



The free iodine colors the mixture brown. Titrate at once with the thiosulfate solution until the brown tinge has become faint, and then add sufficient starch solution to produce a marked blue coloration. Continue the titration cautiously until the last faint lilac tint is entirely removed by a single drop.

The presence of lead or bismuth may change the color of the final tint, but the end point is equally sharp, especially if the last few drops of thiosulfate are allowed to fall into the center of the slowly rotating liquid, and any change from the surrounding surface noted. The reaction between the thiosulfate and the iodine is:



Sodium iodide and tetrathionate are formed.

With low-grade coppers the end point is very sharp, but with high-grade material the large amount of precipitated cuprous iodide usually possesses a faint purplish tinge that is indistinguishable from the last traces of color due to the starch iodide. The addition of a little dilute silver nitrate solution (say 1 ml. of a solution of 100 mg. of silver nitrate in 100 ml. of water) will cause the precipitation of a small amount of silver iodide, the slight yellowish color of which will neutralize the purplish tinge of the cuprous iodide, and thus render the end point of the starch solution appreciably sharper.

See Chapter XXXIII for the preparation and standardization of the solutions.

e. It is best to boil off as much of the free ammonia as possible, before acidifying with acetic acid, in order to avoid the formation of too much ammonium acetate, which has a retarding effect on the reactions of the subsequent titration. The point cannot be told, if much copper is present, by the absence of an ammoniacal odor, as the blue copper ammonium salt gradually decomposes and gives off ammonia. It is usually best to add the acid when the smell of ammonia has become rather faint. Boiling too long does no harm

unless a bluish deposit forms on the flask. This may be copper arsenate or hydroxide, which frequently dissolves with great difficulty in acetic acid. Always look for this deposit before adding the acetic acid, and, when observed, cautiously add enough ammonia to dissolve it, again boiling off any great excess. A precipitate of any nature, due to overboiling, which does not deposit on the flask, will usually do no harm, and the copper contents will subsequently be taken up by the acid. A light-colored flocculent precipitate, sometimes observed in the acetic acid solution, perhaps aluminum hydroxide, is ordinarily without effect. If the cooling, before titration, causes the separation of crystals of copper acetate, they should be redissolved by warming with a little more water and the solution again cooled.

According to the equation previously given, 0.5 gram of copper requires 2.61 grams of potassium iodide. Although direct experiment shows this to be apparently true, yet when only the theoretical amount of potassium iodide is present the reaction is slow, and in fact does not appear to proceed to completion until during the titration, which is thereby unduly prolonged. It is always best, therefore, to use an excess, but as the iodide is expensive the quantity used should be governed by the amount of copper present, which can always be estimated approximately. Allow, say, 1 gram of potassium iodide for every 15 per cent copper, when 0.5 gram of ore is taken for assay. It is convenient to prepare a solution containing 50 grams of potassium iodide in 100 ml. A 2-ml. pipet will thus deliver 1 gram of the salt. No error will be introduced in a doubtful case by adding more potassium iodide after the titration is apparently finished and resuming the operation if the blue color is thereby restored.

The return of the blue tinge in the titrated liquid after long standing is of no significance, but a quick return, which an additional drop or two of the thiosulfate does not permanently destroy, is usually an evidence of faulty work.

However, it is not necessary to begin the determination anew. The following procedure will permit a repetition of the titration: Add 10 ml. of strong nitric acid and heat the mixture to boiling. Heat very cautiously at first until the iodine set free is mostly expelled; otherwise the mixture may foam over. Now manipulate the

flask in a holder over a free flame and boil the solution down as rapidly as desired until only about 5 ml. is left. Dilute with 25 ml. of hot water and boil again for a short time to expel any red fumes. Now add a slight excess of ammonia and finish in the usual manner.³

D. Modifications

Short Iodide Method. To 0.5 gram of the ore in an 8-oz. "copper flask" add 10 ml. of strong hydrochloric acid and 5 ml. of strong nitric acid. Heat gently to decompose the ore, then add 4 ml. of strong sulfuric acid and boil almost to dryness, best over a free flame with the flask in a holder. Allow to cool.

Add 50 ml. of water and heat to boiling, then add 5 ml. of strong bromine water and boil until all the bromine is expelled. By this time all anhydrous ferric sulfate should be in solution.

Remove from the heat and cautiously add strong ammonia until its effects are plainly apparent, by a partial precipitation of ferric hydroxide or otherwise, but avoid an unnecessary excess.

Now add 7 ml. of glacial acetic acid, or sufficient to render the solution strongly acid. Boil for about half a minute and then cool completely under the tap.

Add 2 grams (usually roughly measured after trial) of powdered sodium fluoride, and then, after mixing, 4 ml., more or less, of potassium iodide solution containing 50 grams in 100 ml.

Titrate with standard sodium thiosulfate solution (about 19.5 grams per liter) until the brown iodine color is faint, then add a little starch liquor and continue the titration until the last drop, falling into the center of the nearly quiescent liquid in the flask, produces no further decolorization. It is best to read the buret just previous to this last drop trial, as the addition may prove to be unnecessary.

It is usually safer to add now a little more potassium iodide, to see whether the operation is actually finished, and continue the titration if the additional iodide causes a return of the blue tinge.

³ A simple method of determining the true end point, when it has been slightly passed, is as follows: Add, from a buret, a counted number of drops of permanganate, of any strength, until the color returns. Continue the titration carefully to the end and take reading of buret. Now add the same number of drops of permanganate as before, and again titrate and take reading. Subtract the amount of thiosulfate last required from the previous reading to obtain the true reading.

The following elements do not interfere: As, Sb, Sn, Hg, Zn, Cd, U, Ni, Co, Fe, Mn, Bi, Mo, Ag, Pb. Vanadium interferes. Chromium interferes by forming an insoluble anhydrous sulfate which holds copper. It similarly interferes in the long method. The trouble may be avoided by using no sulfuric acid in the decomposition.

A noticeable feature of this short method is the larger excess of potassium iodide required. This is apparently due to the larger excess of salts in solution than in the long method these salts retarding the reactions. Certain elements appear to show this effect more than others, especially Ni, Co, Mo, and U.

II. ELECTROLYTIC METHOD

A. Application

The electrolytic method is a very accurate procedure, but is limited to materials containing appreciable amounts of copper and few interfering elements. The chief difficulty encountered is the removal of impurities that deposit with the copper. Complex ores requiring many preliminary separations are more conveniently handled by volumetric procedures.

B. Interfering Elements

Practically all the elements of the hydrogen sulfide group cause interference by contaminating the deposit of copper. Arsenic, if present only in small amount, will not deposit with the copper; therefore, if the deposited copper is darkened with arsenic, it usually suffices to redissolve it in nitric acid and deposit it once more.

C. Procedure

a. To 1 gram of the ore in an 8-oz. flask add 10 ml. of strong hydrochloric and 5 ml. of strong nitric acid. Boil gently until decomposition is complete, using more of the acids if necessary. If the evaporation of the liquid causes a separation of soluble salts, add enough hydrochloric acid at the end to bring them into solution again. Finally, add 8 ml. of strong sulfuric acid and boil, best over a free flame, to abundant fumes. After cooling, boil with about 30 ml. of water for a moment and then allow to stand, hot, until any anhydrous ferric sulfate has entirely dissolved. If silver is likely to be present add a single large drop of strong hydrochloric

acid just previous to the boiling, to precipitate it as chloride. Filter, washing filter and residue at least six times with hot water. Dilute the filtrate to about 300 ml. (the dilution is unnecessary if the amount of copper is small), and pass in hydrogen sulfide until all the copper is precipitated, as shown by the clear condition of the supernatant liquid. Filter off the sulfides, washing well with hydrogen sulfide water. Now rinse the precipitate back into the beaker as completely as possible, with hot water, place the beaker under the funnel and pour through the funnel a hot mixture of 5 ml. of a moderately strong colorless solution of sodium sulfide and 15 ml. of water. Remove the beaker, stir the contents well, and, either immediately or after warming a few minutes, according to the amount of arsenic and antimony apparently present, filter through the last filter again. A second extraction is rarely necessary. Wash out the beaker with hot water and then wash the precipitate well with hot dilute sodium sulfide solution. Reserve the filtrate, which almost invariably contains a little dissolved copper. Rinse the residue back into the beaker with hot water, using as little as possible. It is difficult to get the filter very clean, and it is not necessary.

Place beaker and contents once more under the funnel and pour through the funnel a hot solution of about 2 grams of potassium cyanide in about 15 ml. of water. Remove the beaker and replace it with the original flask. Heat and stir the mixture in the beaker until all the copper sulfide is dissolved, adding more potassium cyanide if required, but avoiding a great excess. Sulfides of bismuth, cadmium, etc., will remain undissolved. Again filter through the last filter and wash ten times with hot water. Use small washes each time to avoid a bulky filtrate.

Remove the flask and filtrate to a hood, add 5-6 ml. of strong sulfuric acid (this is usually a sufficient excess), heat to boiling, and boil to fumes. Finally, finish over a free flame until nearly all the excess of acid is expelled. Allow to cool with the flask inclined, to prevent the cake which may form from cracking the glass. The addition of a little nitric acid to the sulfuric acid mixture causes a more rapid solution of the copper sulfide, but this is a disadvantage, as the mixture is then likely to bump badly. Dissolve the cool cake or residue in about 25 ml. of water.

During these operations attention may be turned to the reserved

filtrate, which usually contains an appreciable amount of copper. Acidify it with hydrochloric acid, stir well to coagulate the precipitated sulfur, filter, and wash with hydrogen sulfide water. Ignite the filter and contents in a platinum dish at a dull-red heat until the carbon of the paper is entirely consumed. Be very careful to do this at as low a temperature as possible. All the arsenic and antimony will be expelled. Warm the residue with a few drops of nitric acid, and add the solution to the main portion in the flask. Now add 3 ml. of strong nitric acid, transfer the solution to a suitable beaker, dilute, and electrolyze as described below.

b. The solution should have a volume of about 125 ml. and contain several milliliters of strong nitric acid (sp. gr. 1.42). The amount of free nitric acid necessary is not narrowly limited. It is gradually changed to ammonia by the electrolysis, and therefore, if too little is present, the solution may become alkaline. On the other hand, too much acid retards or may prevent the deposition of the copper. Use an excess of about 3 ml. in the above volume of liquid, but 7 or 8 ml. may be safely employed, with the advantage of preventing, in a large measure, the deposition of any arsenic that may have escaped extraction.

The following apparatus may be used: A cathode consisting of a plain platinum cylinder 5 cm. long and 2.5 cm. in diameter. It has a total surface of about 78.5 sq. cm. and weighs about 12.5 grams. It is supported by a strong platinum wire attached to the top. An anode consisting of a stout platinum wire rising from the center of a base is made by coiling the wire around itself closely so as to form a circular disk. It weighs about 8.5 grams. A beaker suitable for the above electrodes, having a diameter of about 5 cm. and a height of about 8-9 cm.

The volume and acidity of the solution having been properly adjusted, the cathode is cleaned, ignited, and weighed. Now by means of the supports and binding-posts, adjust the electrodes and beaker of solution as follows: Place the anode within the cathode with its base perhaps a quarter of an inch below the lower edge of the cylinder. Adjust the beaker and volume of solution so that the anode nearly touches the bottom of the beaker, and the top of the cathode cylinder is about a quarter of an inch above the surface of the liquid. Cover the beaker with the split watch glass and connect

the electrodes with the battery. For copper, nickel, and bismuth the cathode is to be connected with the zinc pole.

Now include the ammeter in the circuit and note the reading. It is not sufficient to know simply the amount of current passing, since the actual effect of this current in the solution is governed by the area of electrode surface over which it is distributed. The current density should be $ND_{100} = 0.5-1$ ampere.⁴ Electrode tension, 2.2-2.5 volts. Temperature, 20°-30° C. Time required, four to five hours.

When the solution has become colorless and the copper is apparently all deposited, test a drop of the electrolyte with a drop of hydrogen sulfide water, to see whether the copper has been completely deposited. Finally, at the end, lower the beaker from the electrodes, with the current still passing, and at the same time rinse off the adhering acid solution with a stream from the wash bottle. Immediately replace the beaker with another of distilled water, and then stop the current. Remove the cathode, and wash off the water with alcohol. Allow to drain a moment on filter paper, and then dry at about 100° C., cool to room temperature, and weigh. The excess over the original weight of the electrode represents the copper in the weight of ore taken.

⁴ It is necessary to have a certain amount of current passing into a unit area of cathode surface in order to effect a proper deposition of metal; in other words, the current must have a certain *density*. One hundred square centimeters has been chosen as the unit area to which to refer the current as read in amperes. Thus, if a current of 2 amperes is received on 200 sq. cm. of cathode, the current density per 100 sq. cm. is only 1 ampere. Conversely, if 1 ampere of current is passing through 50 sq. cm. of cathode surface the density per 100 sq. cm. is 2 amperes. The symbol ND_{100} is used to express the density of the current per 100 sq. cm. of electrode surface exposed to its action. When the area of the cathode (including both sides) actually immersed in the solution is known, the current density may be easily calculated from the reading of the ammeter. Thus, if the ammeter reads 2 amperes and the cathode has 75 sq. cm.

of surface immersed, then $ND_{100} = \frac{2}{0.75}$, or 2.66 amperes.

If one cell fails to give a sufficient current, use two or three in series, as necessary. Under given conditions of resistance a certain electrode tension is required in order to obtain a stated strength of current. This tension may be measured with the voltmeter. The instrument is not, like the ammeter, included in the main circuit, but is placed in a shunt between the electrodes or points in the circuit whose difference of potential is to be measured.

The proper current conditions having been attained, it is best to leave the ammeter in the circuit during the entire electrolysis, so that any variation in the current may be noted and corrected if necessary.

It is always a good plan to clean the electrode again with nitric acid, and, after igniting and weighing it, replace it once more in the solution and electrolyze for a short time to make certain that all the copper is removed.

D. Modifications

a. *Simpler Electrolytic Method.* The main trouble encountered in the electrolytic method is the removal of impurities that might deposit with the copper. The method just described, though accurate, is long and tedious. A much simpler method, which will ordinarily suffice, is as follows:

Proceed with 1 gram precisely as in the regular iodide method, I, C, removing silver, however, as in II, C, a, until the washed precipitated copper on the filter is ready to be dissolved in nitric acid; or by the thiocyanate method, III, C, until the washed precipitate of CuCNS is obtained. Now remove the filter, wrapping it around the precipitate, and place the whole in a small porcelain crucible. Ignite gently until the paper is consumed, and then heat to redness for half an hour or more, avoiding such an intense heat as might melt the oxide of copper formed. Such impurities as arsenic and antimony are to a large extent volatilized. Finally, allow to cool, pour a little nitric acid in the crucible, and warm gently until all the copper is dissolved. Transfer the solution to the beaker used for electrolysis, bring to the proper conditions (C, b), and electrolyze as usual.

b. *Electrolytic Slimes.* In samples containing arsenic, antimony, tellurium, and selenium, such as electrolytic slimes, add 100 mg. of iron to the nitric acid solution of the sample from which silver has been removed as chloride. Add ammonia to precipitate iron and still have the solution acid. Bring to a boil, settle, filter off the iron precipitate, redissolve it, and again precipitate as before. A third precipitation may be necessary to be certain of having all the copper in solution. Combine the filtrates, evaporate sufficiently, add nitric acid, and electrolyze. The iron precipitate holds the arsenic, antimony, tellurium, and selenium.

c. *Converter Copper.* Dissolve 0.5 gram in 8 ml. nitric acid, 8 ml. water, and 1 ml. sulfuric acid, keeping the beaker covered during solution. When solution is complete and the fumes expelled, dilute with water and electrolyze.

In the copper determinations on mattes and converter copper, the percentage of silver, as determined by fire assay, is deducted from the combined percentages of copper and silver found by electrolysis (291.66 oz. = 1 per cent). The silver may be precipitated with just sufficient dilute sodium chloride solution, an excess being carefully avoided, and, after the silver chloride has been filtered off, the copper may be deposited alone.

d. *Mattes*. Moisten 1 gram of the sample with a few drops of water; add 8 ml. of nitric acid and 1 ml. of sulfuric acid. Run to dryness on steam bath. Take up with water and 8 ml. of nitric acid. Filter and electrolyze.

e. *Slags*. Decompose 2 grams in a platinum dish with 8 ml. nitric acid, 8 ml. hydrofluoric acid, and 1 to 2 ml. sulfuric acid. Evaporate to sulfuric acid fumes. Take up with water and 10 ml. of nitric acid and electrolyze.

f. *Sulfide Ores*. Weigh 1 gram of the sample into a beaker (3½ in. high and 2¼ in. in diameter). Add 8 ml. of nitric acid and a little potassium chlorate. Evaporate to complete dryness on the steam bath. Take up with water and from 6 to 10 ml. of nitric acid. Dilute sufficiently, allow to settle, and then electrolyze.

g. *Oxidized Ores*. Take 1 gram of the sample. Evaporate to dryness with 8 ml. of nitric acid. Add 10 ml. of hydrochloric acid and 2 ml. of sulfuric acid, and evaporate to sulfuric acid fumes. Take up with water and 8 ml. of nitric acid, dilute sufficiently, settle, and electrolyze.

III. VOLUMETRIC THIOCYANATE—IODATE METHOD ⁵

A. Application

This method compares favorably with the iodide method and is applicable to a wide variety of ores.

B. Interfering Elements

Of the elements contaminating the precipitate of CuCNS under the prescribed conditions, lead and silver are the most frequently encountered; mercury, selenium, tellurium, and the precious metals are occasionally met with. Elements that hydrolyze readily, such

⁵ S. W. Parr, *J. Am. Chem. Soc.*, 22, 685, 1900; G. S. Jamieson, *Volumetric Iodate Methods*, Reinhold Publishing Corp., 1926.

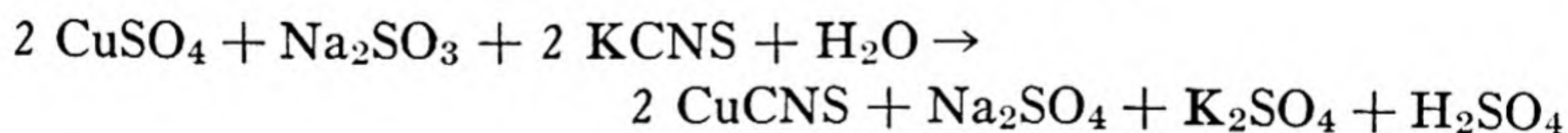
as bismuth, antimony, tin, columbium, and tantalum, may be held in solution by tartaric acid.

C. Procedure

a. Decompose 0.5 to 5 grams of the ore in a 400-ml. beaker, as described under I, C, a. Dilute the cooled sulfuric acid mixture with 50 ml. of water. If very large amounts of iron are present, the copper is best separated by precipitation with hydrogen sulfide, filtered from the iron, and the filter paper and precipitate taken to fumes with 5 ml. sulfuric acid and enough nitric acid to destroy the carbon. Cool and dilute with 50 ml. of water. In the presence of bismuth, antimony, or tin, 2 or 3 grams of tartaric acid should be dissolved in the water. Add enough hydrochloric acid to precipitate any silver as the chloride. Warm the solution until all the soluble salts are dissolved and filter if silver chloride or lead sulfate is precipitated or large amounts of insoluble matter are present.

Add ammonium hydroxide to the filtrate until the iron present is precipitated or the solution turns blue, then carefully clear the solution with 1 : 1 sulfuric acid and add just 2 ml. in excess.

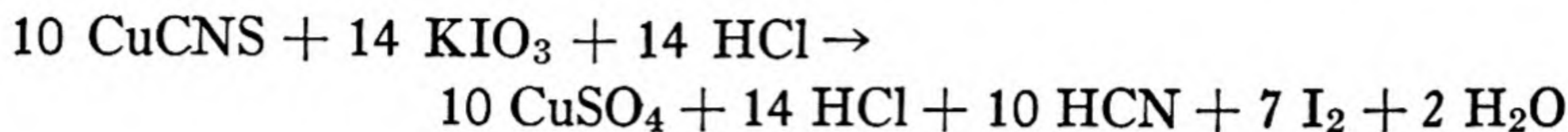
b. Dilute the solution to about 100 ml. and heat to boiling. Remove from the hot plate, and add 1 gram of sodium sulfite by small pinches while stirring vigorously. Replace on the hot plate, and warm until the solution is completely reduced and becomes light blue in color. Add, slowly, from 5 to 15 ml. of a 10 per cent solution of potassium thiocyanate, by means of a dispensing pipet, avoiding a large excess. Copper is precipitated as white cuprous thiocyanate according to the following reaction:



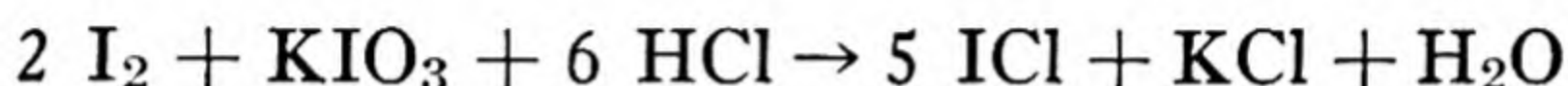
Stir in a little paper pulp, heat to boiling, and set back on a cooler part of the plate until the precipitate coagulates and settles. Filter through a close paper, and wash carefully with hot water.

c. Transfer the precipitate and filter paper to an iodine flask containing a cold mixture of 30 ml. hydrochloric acid, 20 ml. water, and 5 ml. carbon tetrachloride. Shake the flask to break up the paper, and titrate with a standard solution of potassium iodate. (See Chapter XXXIII.) The potassium iodate solution

should be added slowly, the glass stopper being replaced and the flask agitated vigorously after each addition. The solution will become gradually browner in color owing to the liberated iodine.



On continued addition of the potassium iodate the free iodine is converted to iodine monochloride.



On approaching the end point, the solution changes to a greenish yellow color, the last portions of free iodine being absorbed by the carbon tetrachloride, producing a pink color. The iodate solution is then added a drop at a time, with brisk shaking, until the last pink color is discharged from the CCl_4 .

IV. CYANIDE METHOD

A. Application

This method serves for rapid routine technical analyses. The copper is obtained in a blue ammoniacal solution, and its amount is estimated from the quantity of standard solution of potassium cyanide required to discharge the blue color. The results of the cyanide titration are exact if certain conditions are always maintained. It is found that, for the same amount of copper:

1. A concentrated solution requires more cyanide for decoloration than a dilute solution.

2. A hot solution requires less cyanide than a cold one.

3. Whenever, from a rapid addition of cyanide, the color has become rather faint, it may, by simple standing, continue to fade, and perhaps entirely disappear.

4. If the amount of cyanide added is insufficient to effect complete discharge of color, even after allowing the copper solution to stand for several minutes, the titration may then be finished without alteration of the final result.

It is evident from the foregoing facts that in order to obtain correct results the titrations for unknown amounts of copper must be made under conditions that do not differ materially in the fol-

lowing particulars from those governing the standardization of the cyanide solution:

1. Temperature.
2. Rapidity of the final additions of cyanide.
3. Final volume of solution.

B. Interfering Elements

Besides the physical conditions just enumerated, there are chemical conditions that affect the result, as presence of a large amount of chlorides, a large excess of ammonia, etc. Such abnormal conditions require no special consideration, since all are easily avoided by following the method to be described.

C. Procedure

Treat 1 gram, or 0.5 gram if the material seems to contain 40 per cent or over, in an 8-oz. flask with 10 ml. of strong nitric acid. Boil gently until decomposition appears to be complete, and then add about 7 ml. of strong sulfuric acid and heat the mixture over a free flame until all the nitric acid is expelled and the residuary sulfuric acid is boiling freely and evolving copious fumes. Remove from the flame and allow to cool. Ores that are not decomposed by this treatment must be attacked in some special manner for which no general directions can be given. Sometimes the addition of hydrochloric acid is all that is necessary. It is always advisable not to add the sulfuric acid until the ore appears to be well decomposed.

To the residue in the flask add 20 ml. of cold water, and heat the mixture to boiling. If the ore is likely to contain an appreciable amount of silver, add a single drop of strong hydrochloric acid and agitate the liquid so as to collect the silver chloride in clots. One per cent of silver, or 292 oz. per ton of 2000 lb., will increase the apparent copper contents about 0.29 per cent. Allow to stand, hot, until any anhydrous ferric sulfate is entirely dissolved, and then filter, washing flask and filter with hot water. Return the filtrate to the original flask. The volume of the solution should not much exceed 60 ml. at this point. Now place in the flask three pieces of stout sheet aluminum, each about $1\frac{1}{2}$ in. long by $\frac{5}{8}$ in. wide, and heat the mixture to boiling. Boil for perhaps five or ten minutes, according to the volume of the liquid and the appearance

of the aluminum. When all the copper is precipitated the aluminum will usually appear bright and clean, or it will become clean by agitating the flask so as to loosen the adhering copper. Remove from the lamp, add about 15 ml. of strong hydrogen sulfide water, which will insure the complete precipitation of the copper, allow to settle a moment, and then decant through a 9-cm. filter, retaining in the flask the aluminum and as much of the copper as possible. Wash the precipitated copper two or three times by decantation with weak hydrogen sulfide water, using about 25 ml. each time and pouring through the filter. Drain the flask as completely as possible the last time. Now place the flask under the funnel and pour through the funnel 10 ml. of a warm mixture of equal volumes of strong nitric acid and water. Do not wash the filter at this point, but remove the flask and replace it with a beaker. Shake the acid about in the flask gently, so as to dissolve all the copper, warming slightly if necessary, but avoid heating more than is required to just dissolve the copper, or the aluminum may be attacked. When solution is complete, pour the entire contents of the flask into the beaker that was placed under the funnel, washing only the lip of the flask, and then pour the solution back into the flask again, retaining the aluminum in the beaker. Wash the aluminum thoroughly, and then replace the flask under the funnel. Now pour into the filter 5 ml. of a cold saturated solution of bromine in water, and when it has run through wash the filter with hot water. The bromine is to cleanse any dark sulfur left from the copper sulfide on the filter. In the above operations avoid increasing the bulk of the solution more than necessary. Boil the solution in the flask until the bromine is expelled, then cool somewhat and add 10 ml. of strong ammonia (sp. gr. 0.90), and then continue the cooling to room temperature. Titrate the cool solution with the standard cyanide solution cautiously until the blue color is discharged to a considerable extent and it is evident that the end point is not far off.

It frequently happens at this point that the liquid is more or less cloudy. If so, it should, for accurate work, be filtered. If the titration has been carried too far before filtration, the faint blue tinge is likely to fade completely away, thus spoiling the assay. On the other hand, if filtered early in the titration, a second milkyiness may develop later. Filter the partly titrated solution through a

12.5-cm. filter. One washing will usually suffice. Finish the titration very carefully on the clear, pale blue solution, precisely as in the standardization, Chapter XXXIII. Toward the end dilute if necessary, so as to obtain a final volume of about 150 ml.

The number of milliliters of cyanide solution required, multiplied by the copper value of 1 ml., will give the weight of copper contained in the amount of ore taken, from which the percentage is readily calculated.

V. COLORIMETRIC METHOD

A. Application

The colorimetric method is applicable only to products containing small amounts of copper, such as slags and tailings. It is based upon the depths of color produced by cuproammonium nitrate, and, with proper precautions, it is a delicate and accurate means of determining small percentages of copper. For accuracy it is necessary to have the conditions under which the comparison or standard solution was obtained, and that of the sample under examination, as nearly identical as possible. Hence, instead of preparing the standards with known quantities of pure copper only, the various other impurities accompanying the copper in the sample are simulated, by using tailing, blast or reverberatory slags, of known copper content in making up the standard comparison solutions. The following methods are modifications of the method of Thorn Smith, and were developed in the laboratory of the Anaconda Copper Mining Company.

B. Preparation of Standards

Blast Slags. Take 3 grams of sample on which the copper has been determined electrolytically, cover with water, add 10 ml. of nitric acid and 1 ml. of hydrochloric acid, and heat a few minutes on the steam bath. Dilute the mixture, after heating with 100 ml. of water, add dilute ammonia in slight excess, and filter into a colorimetric bottle. Wash until the filtrate fills the bottle to the mark. If the electrolytic copper on this sample was 0.20 per cent, this standard is called "B-2." To prepare "B-3" add 0.003 gram of copper to another 3 grams. "B-4" is prepared by the addition of 0.006 gram of copper, and "B-5" by adding 0.009 gram of cop-

per, the copper always being added before the ammonia, and the samples treated as in the preparation of "B-2." If samples low enough in copper to prepare the lowest standards are not at hand, all the copper may be removed electrolytically and then sufficient of a standard copper solution added for the required standard.

Tailings. Heat 1 gram of the sample on the steam bath with 5 ml. of nitric acid and a pinch of potassium chlorate. Dilute, filter, and wash as for slags. If the electrolytic copper on this sample was 0.50 per cent, the standard is called "T-5." To prepare "T-6" add 0.001 gram of copper to another gram sample; 0.002 gram for "T-7"; 0.003 gram for "T-8"; 0.005 gram for "T-10."

Reverberatory Slags. Take 2 grams of sample; add 10 ml. of hydrochloric acid and 2 ml. of nitric acid. Heat, dilute, add ammonia, filter, and wash as for blast slags. If the electrolytic copper on this sample was 0.30 per cent, this standard is called "R-3." For "R-4" add 0.002 gram of copper to another 2 grams of sample. Add 0.004 gram for "R-5"; 0.006 for "R-6"; and so on. Treat each as in the preparation of "R-3."

A set of standards being prepared as above, another set of bottles is arranged, each bottle being filled almost to the mark with water and 10 ml. of ammonia. A standard solution of copper, containing 0.001 gram of copper to the milliliter, is run into each from a buret until the color produced exactly matches a corresponding standard prepared as above. The buret readings are carefully noted.

The following table is an example of results thus obtained:

B-2 required	4.4 ml.	R-2 required	3.2 ml.	T- 3 required	2.8 ml.
B-3	" 6.7 ml.	R-3	" 4.6 ml.	T- 4	" 3.8 ml.
B-4	" 9.1 ml.	R-4	" 6.1 ml.	T- 5	" 4.7 ml.
B-5	" 11.1 ml.	R-5	" 7.9 ml.	T- 6	" 5.7 ml.
		R-6	" 9.7 ml.	T- 7	" 6.6 ml.
		R-7	" 11.4 ml.	T- 8	" 7.6 ml.
		R-8	" 13.2 ml.	T- 9	" 8.5 ml.
				T-10	" 9.5 ml.

By means of this table, standards may be rapidly prepared.

C. Procedure

Treat blast slags, reverberatory slags, and tailings exactly as described in "Preparation of Standards," and match the filtrates with the standards.

Except for converter slag (of which 0.5 gram is taken), all portions are 1, 2, or 3 grams.

Tailings are weighed into No. 1 beakers, 100-ml. capacity, and slags into No. 2 beakers, 200-ml. capacity.

Tailings are treated with nitric acid and a pinch of potassium chlorate, set upon the steam plate and left for half an hour. The addition of nitric acid should be regulated so as to leave about 5 ml. after treatment on the hot plate. After the hot-plate treatment about 25 to 30 ml. of cold water is added to the beakers and they are then placed in front of the color bottles which have been previously arranged. These color bottles are square, to allow of easy and safe handling, and are made of clear white glass. They are $7\frac{1}{2}$ in. high, with a body $2\frac{1}{2}$ in. in diameter and a short neck about $1\frac{3}{4}$ in. in diameter. Ammonia (1 : 1) is added to the beakers in such quantity as to give about the same excess as is used in the standards. Ribbed funnels $4\frac{1}{4}$ in. in diameter are set in the mouths of the bottles and provided with filters $18\frac{1}{2}$ cm. in diameter. The contents of the beakers are now poured "clean" into the filters. The beakers are washed once with warm water, which is then poured through the filters, and, after draining, the precipitate in each filter is given one good wash with warm water. The funnels are now removed, and the bottles are filled up to the standard marks with water. The larger bulk of solution before filtering and the greater amount of wash water required cause the mark on the slag bottles to be higher than that on the tailings. On the bottle described the tailings mark will come about halfway up, and the slag mark will be near the top. The tests, when ready, are matched against the standard colors arranged in a color stand. This stand is made of wood, painted white, and faces a window. Each standard bottle is in a separate compartment, so as not to be affected by the color of an adjacent standard. In making comparisons the standard and the unknown should be at equal distances from the partitions, as the latter have a slight effect on the color.

Results are read and reported to the nearest 0.05 per cent by reading between the standards, which are graduated to 0.1 per cent.

Blast slags decompose easily; reverberatory slags are best decomposed by first adding hydrochloric acid, and then, after a few

minutes' digestion, adding nitric acid. Add a little water before the acid, so as to make a paste, which will prevent caking.

Reverberatory and converter slags should be allowed about three-quarters of an hour on the steam plate, then taken up with water, and stirred thoroughly with a rubber "policeman." The dilute ammonia should be added while stirring, so as to judge best the required excess.

Sometimes the color produced in a test has a greenish tinge, and the test is then likely to be read too high. Heath states that this may be due to the presence of organic matter, which impairs the complete precipitation of ferric hydroxide by ammonia. If the green tint is too pronounced the sample should be ignited.

Standards of low copper content seem to preserve their color best with a small excess of ammonia (5 ml.). Those of higher copper content require 10 to 20 ml. excess. The sample to be matched should be as nearly like the standard in all respects as possible.

FLUORINE MINERALS

Mineral Name	Chemical Formula	% F	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Fluorite.....	CaF ₂	48.9	White or tinted	3.2	Pb, Ag, Zn, Si, Ba, Sn, P, Mg	H ₂ SO ₄ HClO ₄	Na ₂ CO ₃ Na ₂ CO ₃ + KNO ₃
Cryolite.....	Na ₃ AlF ₆	54.4	White or tinted	3.0	Fe, Mn, Si	H ₂ SO ₄	KHSO ₄ , Na ₂ CO ₃
Apatite.....	3 Ca ₃ (PO ₄) ₂ ·CaF ₂	3.8	White or tinted	3.2	Si, Fe, Mn, Ti, Mg, Na, K, Cl	HCl HNO ₃	

Fluorine may be encountered quite often in the gangue minerals of many ores. Those minerals completely or partly decomposed by acid digestion, such as ilvaite, wavellite, wagnerite, amblygonite, triplite, vesuvianite, humite, chondrodite, and norbergite, will leave part or all of the fluorine in solution and will probably cause trouble in the analysis. When decomposition is accomplished by an alkaline fusion, minerals like topaz, tourmaline, hornblende, and augite will leave fluorine in solution as a soluble alkaline fluoride. Fluorine as an interfering element is usually removed by repeated fuming with either sulfuric or perchloric acids.

CHAPTER XIV

FLUORINE

I. LEAD CHLOROFLUORIDE METHOD ¹

A. Application

The method of Berzelius has long been the best procedure for the determination of fluorine, but it is both tedious and time-consuming. The following method, developed by the Bureau of Standards, is a modification of the above and will serve very well for most purposes. It is suitable for the determination of fluorine between limits of 0.01 to 0.10 gram. Below 0.01 gram the results have a tendency to be slightly low, and above 0.10 gram they tend to be slightly high.

B. Interfering Elements

Aluminum, iron, large quantities of alkali salts, and boric oxide retard or prevent the complete precipitation of lead chlorofluoride. Of these, the first two are by far the most troublesome. The effect of the last two can be minimized by letting the solution stand for a longer time. Boron has a greater effect when the quantity of fluorine is large than when it is small. Small quantities of silica, ammonium nitrate, phosphoric acid, sulfuric acid, and chromic acid have little or no harmful effect if lead chlorofluoride is precipitated under the conditions prescribed, and the chlorine is titrated as in Volhard's method.

C. Procedure

a. Fuse 0.5 gram of the sample (dried at 105° C.) with 6 grams of potassium carbonate, leach the cooled melt with hot water, and filter when disintegration is complete. Wash the insoluble residue thoroughly with hot water, and adjust the volume of the filtrate

¹ J. I. Hoffman and G. E. F. Lundell, *Bur. Standards J. Research*, 3, 581, 1929, by permission of Dr. Lundell.

and washings to approximately 200 ml. Add 1 gram of zinc oxide dissolved in 20 ml. of dilute nitric acid (1 : 9), boil for one minute with constant stirring, filter, and wash thoroughly with hot water.

b. To the filtrate add 2 drops of brom phenol blue indicator and 3 ml. of a 10 per cent solution of sodium chloride. Adjust the volume of the solution to 250 ml., add dilute nitric acid until the color changes to yellow, and then add dilute sodium hydroxide until it just changes to blue. Now add 2 ml. of dilute hydrochloric acid (1 : 1) and 5 grams of solid lead nitrate, $\text{Pb}(\text{NO}_3)_2$, and heat on the steam bath. As soon as the lead nitrate is in solution, add 5 grams of solid sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}$, stir vigorously, and digest on the steam bath for one-half hour with occasional stirring. Allow to stand four hours at room temperature, and decant the solution through a paper of close texture. Wash the precipitate, beaker, and paper once with cold water, then four to five times with a cool saturated solution of lead chlorofluoride,² and then once more with cold water.

c. Transfer the precipitate and paper to the beaker in which the precipitation was made, stir the paper to a pulp, add 100 ml. of dilute nitric acid (5 : 95), and heat on the steam bath until the precipitate is dissolved (five minutes is ample). Then add a slight excess of a 0.2 *N* solution of silver nitrate, digest on the steam bath for one-half hour, cool to room temperature while protected from the light, filter, wash with cold water, and determine the silver nitrate in the filtrate by titration with a standard solution of potassium thiocyanate (standardized against the silver solution), using 5 ml. of a solution of ferric alum as the indicator. Subtract the amount of silver nitrate found in the filtrate from that originally added. The difference will be that required to combine with the chlorine in the lead chlorofluoride, and from this the fluorine may be computed. One milliliter of 0.2 *N* silver nitrate is equivalent to 0.00380 gram of fluorine.

² (a) Dissolve 10 grams of lead nitrate in 200 ml. of water; (b) dissolve 1 gram of sodium fluoride in 100 ml. of water and add 2 ml. of concentrated hydrochloric acid; and (c) mix solutions (a) and (b). Allow the precipitate to settle, and decant the supernatant liquid. Wash four or five times with 200 ml. of water by decantation, and then add about 1 liter of cold water to the precipitate and allow to stand for one hour longer with occasional stirring. Pour through a filter, and use the clear filtrate.

IRON MINERALS

Mineral Name	Chemical Formula	% Fe	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Hematite.....	Fe_2O_3	70.0	Bright red to reddish brown	5.2	Ti, Mn, Si, S, Ca, Mg	HCl (Difficultly)	Na_2CO_3 , KHSO_4
Limonite.....	$\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$	Variable	Yellow to orange or brown	3.8	Ti, Mn, Si, S, Ca, Mg	HCl	Same
Goethite.....	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	62.9	Yellow to brown	4.3	Ti, Mn, Si, S, Ca, Mg	HCl	Same
Magnetite.....	$\text{FeO} \cdot \text{Fe}_2\text{O}_3$	72.4	Black	5.2	Ti, Mn, Ni, Si, Ca, Mg	HCl	Same
Siderite.....	FeCO_3	48.2	White to yellowish or brownish	3.8	Ca, Mg, Mn, Pb, Si	HCl	Same
Pyrite.....	FeS_2	46.6	Black, metallic luster	5.0	Practically all metals	HNO_3	
Arsenopyrite..	FeAsS	34.4	Grayish black, metallic luster	6.0	Co, Ni, Pb, Zn, Cu, Sn, W	HNO_3	
Chalcopyrite..	$\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$	30.5	Greenish black, metallic luster	4.2	Practically all metals	HNO_3	
Pyrrhotite....	$\text{Fe}_{n+1}\text{S}_n$	Variable	Grayish black, metallic luster	4.6	Ni, Cu, Mg, Al	HNO_3	
Franklinite...	$(\text{FeZnMn})\text{O} \cdot (\text{FeMn})_2\text{O}_3$	Variable	Reddish brown to brownish black	5.1	Ca, Mg, Pb, As, P, S	HCl	Na_2CO_3 , KHSO_4
Chromite.....	$\text{FeO} \cdot \text{Cr}_2\text{O}_3$	24.9	Yellow to gray to dark brown	4.5	Ca, Mg, Al, Si, Mn	$\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4 + \text{HClO}_4$	Na_2O_2
Ilmenite.....	$\text{FeO} \cdot \text{TiO}_2$	36.8	Reddish brown to brownish black	4.7	Mg, Al, Si, Mn	Na_2CO_3 , KHSO_4
Wolframite...	$(\text{FeMn})\text{WO}_4$	Variable	Dark brown to black	7.2	Sn, B, F, Ca, Mg	Aqua regia	Na_2CO_3
Marcasite....	FeS_2	46.6	Greenish black, metallic luster	4.9	Si, Cu, Pb, Zn, Ca, Mg, Ba, As, Co, Ni, Ti	HNO_3	

Iron is almost always encountered in ore analysis. In general, decomposition may be effected by acid attack, followed if need be by fusion of the insoluble residue. A few minerals such as staurolite, chromite, and cassiterite require special treatment.

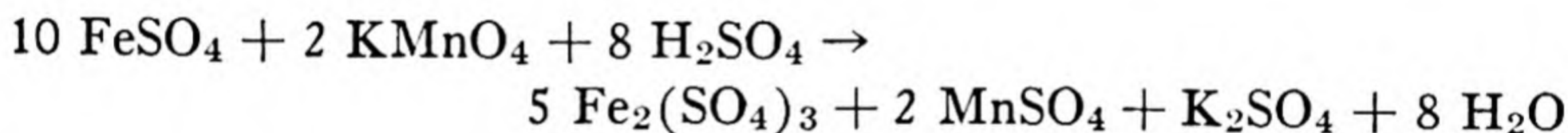
CHAPTER XV

IRON

I. PERMANGANATE METHOD

A. Application

In the determination of iron in ores and metallurgical products some modification of either the permanganate or dichromate volumetric method is ordinarily employed. Both methods give exact results, and the choice of the one to use generally depends on the personal preference of the operator. The permanganate method is especially applicable to sulfuric acid solutions of the iron or solutions obtained after fusions with potassium bisulfate. The reduced iron salt is oxidized to the ferric condition according to the following reaction:



B. Interfering Elements

Titanium, vanadium, chromium, molybdenum, tungsten, and uranium are reduced along with iron by zinc in sulfuric acid solution. Titration in cold solution with *o*-phenanthroline indicator eliminates interference by chromium and vanadium. Materials containing titanium or uranium may be handled by reducing the iron with sulfur dioxide or by the Zimmerman-Reinhardt method. A preliminary separation of iron by ammonium hydroxide removes molybdenum and tungsten and is usually a desirable procedure as a means of eliminating insoluble material, copper, etc.

Ores containing a large amount of arsenic will frequently give low and variable results, and the titration will have a rather quickly fading end point. Apparently, some arsenic has been left in solution, after the reduction, in the *ic* condition, and this, by subsequently oxidizing iron, makes the results low, as the arsenious acid produced is only very slowly acted upon by the permanganate. The addition of cupric sulfate solution usually prevents this trouble by

precipitating metallic copper on the zinc, which in turn precipitates the arsenic as copper arsenide. The zinc alone cannot be depended upon to do this.

C. Procedure

a. Weigh 0.5 gram of the ore and place in a 250-ml. beaker. Decompose with acids according to the nature of the sample. It is usually best to begin with 10 ml. of strong hydrochloric acid and warm gently as long as decomposition appears to progress, adding more acid if necessary. If undecomposed sulfides remain, add 5 ml. of strong nitric acid and continue the heating. Note whether this insoluble residue now appears white or discolored. If discolored, endeavor to effect a better decomposition by continued gentle heating with hydrochloric acid. Finally, add to the mixture (which should not be so concentrated as to contain separated salts) about 5 ml. of strong sulfuric acid and heat until practically all the acid, including the sulfuric, is expelled.

Allow to cool, add 30 ml. of cold water and 10 ml. of strong hydrochloric acid, and warm to dissolve all soluble salts. Examine the insoluble residue for yellow tungstic acid. The solution may be tested at this point for arsenic, molybdenum, uranium, etc., by the methods given in Chapter I. A green solution indicates the possible presence of copper, vanadium, chromium, or nickel. If interfering elements are noted, make the solution decidedly alkaline with ammonium hydroxide, add a little bromine water, boil a few minutes, and filter on a rapid paper, washing with hot water, rinse the precipitate back into the beaker, and dissolve in 5 ml. of hydrochloric acid. Pour the dissolved iron back through the same paper, catching the solution in a clean 250-ml. beaker. Wash well with hot 1 : 1 hydrochloric acid and finally with hot water.

If hydrochloric acid alone effects a solution of all the iron in the ore, the further treatment with nitric or sulfuric acid is unnecessary. In order to have the right amount of acid finally present, boil the solution nearly to dryness and then add 8 ml. more of hydrochloric acid and dilute to 40 ml. with cold water.

b. *Treatment of Silicates and Other Refractory Substances.* The acid treatment just described will serve excellently for the decomposition of most ores treated at western lead-smelters, but

silicates, furnace products, refractory oxides, etc., are frequently encountered that do not thus yield up all their iron. In the purchase of ores for lead-smelters the actual total iron contents are not, as a rule, absolutely required, but only what is obtained by the acid treatment. In most analyses practically all the iron is thus dissolved. What remains is classed with the insoluble residue or "silica." Whenever the total iron is required the material must, of course, be completely decomposed. Silicates, or mixed material containing silicates, may be decomposed as described under Silica. The nature of the material has to be considered in deciding upon the best course to pursue, and the matter of the decomposition is fully explained in the section referred to. An acid solution of the iron is thus finally obtained.

c. Method That Is Frequently Effective When Acids Fail. Weigh 0.5 gram of the finely ground material into an 8-oz. flask. Add 5 grams of dry sodium sulfate and about 6 ml. of strong sulfuric acid. Manipulate the flask in a holder over a strong naked flame, boiling off all the acid and finally reducing the residue to a nearly or actually red-hot melt. Do this final heating with the melt on the side of the flask, so as not to bulge the bottom. Cool with the flask on its side, in order that the contracting cake will not crack it, or distribute the melt around the sides of the flask until it solidifies. This treatment will effect a complete decomposition of many refractory ores, either sulfides or oxides. Silicates may not be much attacked. If undecomposed particles remain that are likely to contain iron, the following procedure may be tried: Add 10 ml. of water to the cooled mass and about 6 ml. of sulfuric acid. Heat until the cake has dissolved or disintegrated, then add hydrofluoric acid, about as much as can be held in an ordinary platinum crucible cover, and repeat the previous treatment over a naked flame. The flask will not be materially attacked and the glass is not likely to contain iron in sufficient amount to affect the determination. If this treatment still leaves a dark insoluble residue, one more effort may be made on the same portion. To the cool mass add water and sulfuric acid and disintegrate as before. Now add one-eighth of a 9-cm. filter paper and again run down over the flame until the carbon is entirely burned off and a melt once more obtained, then cool as before. Antimonial compounds will frequently yield to

this treatment (owing to the reduction of the antimony to the *ous* condition) where the other methods fail.

If a satisfactory decomposition has been attained, add 30 ml. of water and 10 ml. of hydrochloric acid to the cool mass and warm gently to dissolve the cake. Continue as described in g.

d. *Decomposition of Silicates by Hydrofluoric Acid.* Sometimes the iron in a silicate, or a silicious residue remaining after acid treatment, can be quickly dissolved as follows:

Treat the substance in a small platinum dish with equal parts of strong pure hydrochloric and hydrofluoric acids. Warm gently until decomposition appears complete, adding more of the acids if necessary, and then add about 3 ml. of dilute sulfuric acid (1 : 2) and evaporate to white fumes. To the cool residue add a little water and a few drops of hydrochloric acid, and warm to effect solution. If the material is a residue, transfer this solution to the flask containing the original filtrate, make to a volume of about 40 ml., reduce with zinc, and finish as usual (g). If the material is the ore itself the operations are similar but 5 ml. of hydrochloric acid must be added before reduction. When nitric acid has been used in a preliminary treatment it should be expelled before filtration from the residue. The solution for reduction should have a volume of about 40 ml. and contain from 5 to 10 ml. of free hydrochloric acid.

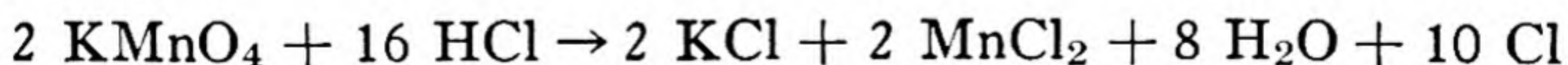
e. *Titaniferous Ores.* If an ore contains an appreciable amount of titanous acid it becomes impracticable to use zinc as a reducing agent, since the TiO_2 in solution is thereby reduced to Ti_2O_3 (which imparts a violet color to the liquid), and this is subsequently oxidized back to TiO_2 again by the permanganate. Thus more permanganate will be required than corresponds to the amount of iron present.

With such titaniferous ores, fuse the sample with potassium bisulfate in a silica crucible. Dissolve the melt in 50 ml. of 10 per cent sulfuric acid, add 5 ml. of sulfurous acid, and heat. Ferric iron is reduced; titanous acid remains unaffected. As the yellow color fades, increase the heat gradually to the boiling point. Continue the boiling until all odor of sulfur dioxide has disappeared and the vapors from the solution give a negative test with potassium iodate-starch paper. Place the beaker in cold water, and, when

the solution is quite cold, transfer it to a large beaker, dilute to 700 ml., and titrate as usual.

f. *Chrome Iron Ore.* Treat as described in **Chromium, I, C, a**, except that a nickel or copper crucible must be used instead of an iron one. After the chromium is filtered off, the iron is left with the residue on the filter as ferric hydroxide. With as little hot water as possible rinse the residue from the filter into a small beaker. Place the beaker under the funnel, and dissolve whatever precipitate still adheres to the filter by slowly pouring through it a warm mixture of 10 ml. strong hydrochloric acid and 15 ml. water. Heat the mixture in the beaker to dissolve all the ferric hydroxide, and determine the iron according to g.

g. To the acid solution of the iron obtained by any of the preceding methods add 6 grams of pure granulated zinc (best about 20 mesh), and 3 ml. of 4 per cent copper sulfate solution if arsenic has been found to be present. The iron is reduced from the ferric to the ferrous condition and hydrogen is liberated by the action of the free acid on the zinc. Allow the reaction to continue until the solution is completely decolorized, heating, if necessary, toward the end if the action is slow. When no separations have been made, the reduced solution, instead of being colorless, may be colored by certain elements as follows: nickel-green, uranium-yellow green, chromium-blue green, vanadium-blue, tungsten-blue, cobalt-pink, titanium-violet, and molybdenum-tan to brown. Now add 50 ml. of cold water to the mixture in the flask, and then 10 ml. of strong sulfuric acid. This will dissolve whatever zinc remains and will also supply the solution with a large excess of sulfuric acid. The sulfuric acid will counteract the otherwise disturbing influence of the hydrochloric acid present during the subsequent titration and secure a sharp end point. Hydrochloric acid and potassium permanganate mutually decompose each other with the evolution of chlorine as follows:



When this takes place during an iron titration, the amount of permanganate consumed is increased, thus producing high results, while the end point is obscured owing to the continual fading of the pink tinge. If, however, the solution is cold, largely diluted, and

contains a proper excess of sulfuric acid, a little hydrochloric acid causes no trouble.

When nearly all the zinc is dissolved the mixture should be filtered. Almost all zinc contains lead as an impurity, and this remains behind as a finely divided black residue, which would cause trouble by consuming permanganate if not filtered off. As the solution has a tendency to clog a filter and run very slowly it is better to filter through a plug of absorbent cotton placed in a funnel and moistened. Do not use an unnecessarily large wad. Place it in the funnel so that the under side is smooth, with the fibers lying horizontally. If the fibers are allowed to string downward they are likely to obstruct the neck of the funnel and cause a slow filtration. The proper arrangement filters rapidly and washes easily. Receive the filtrate in a liter beaker containing an inch or two of water. Wash the filter and residue well with cold water.

Dilute the solution in the beaker with cold distilled water to about 700 ml., having previously placed a mark on the jar at that point. The solution is now ready for titration, which should proceed without unnecessary delay, to avoid oxidation of the ferrous iron by the air. Place a piece of white paper under the jar, in order that the color change may be rendered more distinct, and run in the permanganate solution from a buret while stirring the mixture with a glass rod. The color of the permanganate is almost instantly destroyed at first, but as the end point is approached a less rapid decolorization can easily be detected if the permanganate is added cautiously. Proceed more and more carefully, finally drop by drop, until a very faint permanent pink tinge is obtained. The reaction now being complete, read the buret. Another drop of permanganate should turn the solution decidedly pink.

The use of *o*-phenanthroline-ferrous sulfate¹ as an indicator greatly improves the end point in this titration, the color change being from orange red to bluish green in sulfuric acid solution and from orange red to yellow in hydrochloric acid solution.²

¹ Walden, Hammett, and Chapman, Phenanthroline—Ferrous Ion: A reversible oxidation-reduction indicator of high potential and its use in oxidimetric titrations, *J. Am. Chem. Soc.*, 55, 2649, 1933.

² For information regarding oxidation and reduction indicators, consult *Newer Methods of Volumetric Chemical Analysis*, by E. Brennecke, et al., D. Van Nostrand Co., Inc., 1938.

Multiply the number of milliliters of permanganate used by the percentage value of 1 ml. for iron to obtain the percentage of iron in the sample. See Chapter XXXIII for the preparation and standardization of the permanganate solution.

D. Modification ³

The following solutions are required:

Stannous Chloride. Dissolve 1 pound of stannous chloride in 1 pound of strong hydrochloric acid (1.2 sp. gr.) to which some water has been added, and dilute to 2 liters. Keep in a tightly stoppered bottle with a stick of pure tin metal.

Hydrochloric acid of 1.1 Sp. Gr. Mix equal volumes of the strong acid (1.2 sp. gr.) and water.

Mercuric Chloride. Make a saturated solution in hot water, allow to cool and crystallize, and then filter.

Manganese Sulfate. Dissolve 160 grams in water and dilute to 1750 ml. To this add 330 ml. of phosphoric acid syrup of 1.7 sp. gr. and 320 ml. of sulfuric acid, 1.84 sp. gr. This solution is to obviate the deleterious action of liberated chlorine when potassium permanganate is added to a hydrochloric acid solution containing ferrous iron.⁴

³ Zimmerman-Reinhardt method as modified by Mixer and Dubois. *J. Am. Chem. Soc.*, 17, 405, 1895.

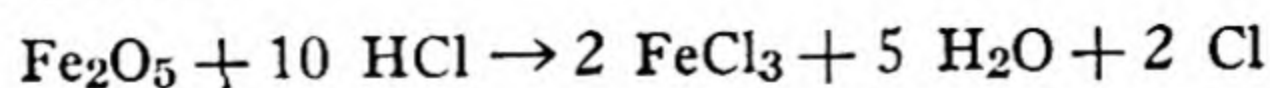
⁴ In regard to the functions of the manganese sulfate, see page 550 of Treadwell-Hall, *Analytical Chemistry*, Vol. II, John Wiley & Sons, Inc., 1935.

Some of the essential points are as follows:

Dilute permanganate solution does not decompose cold dilute hydrochloric acid in the absence of ferrous iron. When ferrous iron is present, however, decomposition occurs, with a noticeable evolution of chlorine. In the presence of only a ferric salt, under similar conditions, there is no decomposition. These facts indicate that there is no direct action of the permanganate upon the hydrochloric acid, and that decomposition of the hydrochloric acid is due to the intermediate formation of a peroxide (Fe_2O_5).

The presence of considerable manganous salt prevents the decomposition that would otherwise occur. It does this by combining, with the excess of oxygen in the intermediate peroxide, more quickly than the oxygen can attack the hydrochloric acid. MnO_2 is formed, which gives up 1 oxygen to ferrous iron to the end. When the oxidation of the ferrous iron is complete, no more MnO_2 will be formed.

If the concentration of the manganous salt is too low, the peroxide salt will decompose hydrochloric acid:



The phosphoric acid allows the formation of iron phosphate, which, being nearly colorless, renders the end reaction more distinct.

Treat 0.5 gram in a small covered beaker with 2.5 ml. of the stannous chloride solution and 10 to 15 ml. of the dilute hydrochloric acid. Boil the mixture very gently on an iron plate until the ore is completely decomposed. For ores running less than 55 per cent of iron it is advisable to use a little less stannous chloride. The solution of the ore is usually very rapid, requiring only a few minutes.

When the ore is dissolved, run a few drops of stannous chloride from a buret into the hot solution until all the iron is reduced to the ferrous state, as indicated by the disappearance of the greenish-yellow color. If an excess of stannous chloride has been originally added, it is, of course, unnecessary to add more. In any case, to avoid too great an excess of stannous chloride, which is undesirable, it is advisable to add a few drops of potassium permanganate solution to the reduced mixture to slightly oxidize the solution once more. The solution, in its slightly oxidized condition, should be kept warm until ready to titrate, and then the final reduction should be made with a drop or two of stannous chloride, avoiding unnecessary excess. Now wash down the sides of the beaker and add, while stirring, 5 ml. of the mercuric chloride solution to take up the excess of stannous chloride. Have ready a 500-ml. beaker containing 6-8 ml. of manganese sulfate solution and about 400 ml. of cold water. Wash the iron solution into this and titrate at once with potassium permanganate in the usual way.

Ores containing organic matter, some magnetites, and pyritous ores require the usual precautions. With ores containing very large amounts of organic matter, it is generally most advantageous to burn off directly and follow the regular method. Ores containing small amounts of organic matter and slightly pyritous ores are dissolved in hydrochloric acid and oxidized with potassium chlorate, after which the regular method is pursued. Heavy sulfides may be treated with nitric acid as described in C, a, and the hydrochloric acid solution eventually obtained may be treated as above. Magnetites should be ground very fine in an agate mortar, and then, if it is impossible to effect complete solution, either the ore or the insoluble residue may be treated as described in C, c.

II. DICHROMATE METHOD

A. Application

Oxidation of the reduced iron solution by potassium dichromate is a useful procedure when the iron is in hydrochloric acid solution. The following method will serve well for the majority of technical analyses.

B. Interfering Elements

See preceding method.

C. Procedure

a. The following solutions are required:

Stannous Chloride. This should be strongly acid and should contain about 15 grams of tin, and 350 ml. of strong hydrochloric acid to the liter. It may be made by dissolving the tin in the acid by the aid of heat and diluting. It is usually more convenient to prepare it from the crystallized stannous chloride as follows: Dissolve 14.5 grams of the crystals in 165 ml. of strong hydrochloric acid and dilute to 500 ml. Keep in a half-liter bottle in which a stick of pure tin is placed to prevent oxidation. One milliliter of this solution will reduce about 0.015 gram of iron from the ferric to the ferrous condition. It will naturally become somewhat stronger as the stick of tin gradually dissolves in the acid liquid.

Mercuric Chloride. Use a saturated solution, and keep an excess of the crystals in the bottle. Such a solution will contain at least 60 grams of mercuric chloride to the liter. About 1.2 ml. of this solution will oxidize the tin in 1 ml. of the above stannous chloride solution, at its original strength, to the stannic condition.

Potassium Ferricyanide. This solution should be dilute, say 0.1 gram in 15 ml. of water. The exact strength is immaterial. It is best made frequently, or when required, in small quantity, as the solution does not keep indefinitely.

Obtain the iron in solution by the methods given in I, C, a, b, or f.

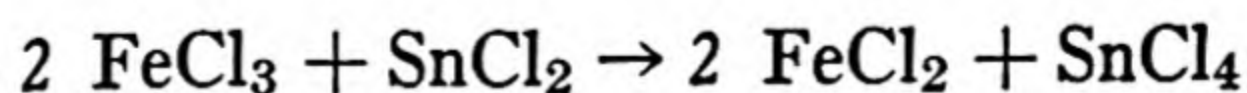
Observe that, whatever method of decomposition is employed, a solution or mixture containing about 5 ml. of free hydrochloric acid is finally obtained.

b. To the mixture in the flask add about 0.2 gram of pure cupric sulfate, or better, an equivalent amount of strong solution,

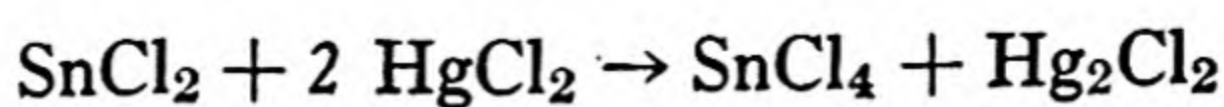
and see that it dissolves. Now add about 20 grams of pure, finely granulated test lead, and boil gently to reduce the iron to the ferrous condition. The copper precipitates on the lead and prevents it from cohering in lumps. If the ore already contains sufficient copper it is, of course, unnecessary to add more. Avoid adding the lead to a boiling-hot solution or it will probably produce a sudden evolution of steam and overflow the flask. The iron is usually entirely reduced by about five minutes' gentle boiling. It is best to boil for a few minutes after the liquid has become completely decolorized. All the copper is thus precipitated and any arsenic or antimony also removed from the solution. Prolonged boiling causes the formation of too much lead chloride, which separates out and renders the solution difficult to filter. Filter boiling hot, bringing the excess of lead upon the filter, and wash thoroughly with hot water.

c. To the hot solution now add the stannous chloride solution cautiously until decolorization is complete, avoiding more than a slight excess. Transfer the reduced solution to a large beaker, washing out the flask with cold water. Add about 10 ml. of the mercuric chloride solution, pouring it in rapidly while stirring the mixture. If only a slight excess of stannous chloride was used, the 10 ml. of mercuric chloride will be ample and a white precipitate will be produced, but if the excess of stannous chloride was large the precipitate may become gray or black from the separation of metallic mercury. This discoloration should be watched for carefully, and if the faintest trace of it appears an abundance of the mercuric chloride solution should be added at once. If this restores the pure white color the test may proceed; otherwise it is spoiled and must be begun anew.

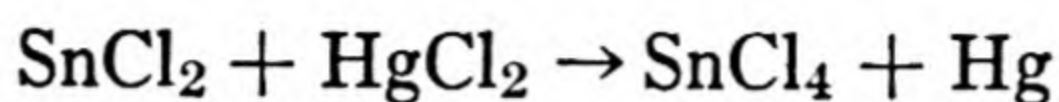
The reactions involved are, first,



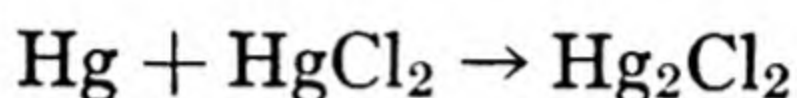
The stannous chloride thus reduces the ferric to ferrous chloride and becomes itself oxidized to stannic chloride. The excess of stannous chloride added, when treated with sufficient mercuric chloride, is oxidized to stannic chloride as follows:



Mercurous chloride is produced, which is a white precipitate. If the excess of stannous chloride is large, however, so that the mercuric chloride added is insufficient for the last reaction, the following takes place:



The finely divided metallic mercury discolors the liquid. If more mercuric chloride be added at once, the mercury may frequently be taken into combination again:



The liquid therefore contains, as a final result, ferrous chloride, stannic chloride, mercuric chloride, and a precipitate of white mercurous chloride. The only one of these compounds affected by the dichromate in the subsequent titration is the ferrous chloride.

d. The mixture in the beaker is now ready for the titration, which should proceed without delay, since after the mercuric chloride has been added there is nothing to prevent oxidation of the ferrous solution. Have ready a glazed porcelain tile coated with a thin film of paraffin. Run in the dichromate solution from the buret while stirring the solution, and from time to time touch a drop of the ferricyanide on the porcelain with a drop of the solution. As long as a large amount of iron still remains in the ferrous condition the ferricyanide will produce intensely blue tests. Continue to run in the dichromate solution thus until the color of the tests becomes fainter. Proceed then with more caution, finally drop by drop, until the test drop flashes yellow-orange and fails to show a blue tint after half a minute. Read the number of milliliters used, and, from the weight of sample taken, calculate the percentage of iron. The preparation and standardization of the dichromate solution are described in Chapter XXXIII.

III. COLORIMETRIC METHOD ⁵

A. Application

The small amounts of iron occurring in ores and concentrates and materials such as glass sand, limestone, kaolin, and potash are best determined by a colorimetric method. The following proce-

⁵ J. W. Mellor, *Trans. Ceramic Soc., England*, 8, 125, 1908.

dure may also be applied to the analysis of reagents for small amounts of iron.

B. Interfering Elements

Fluorides, phosphates, arsenates, and elements giving colored solutions interfere.

C. Procedure

The least manipulation possible is recommended in preparing the solution for comparison, owing to the presence of iron in practically all materials and reagents. A blank determination should always be run side by side with the sample. Digest 0.5 gram or suitable amount of the sample in a clean platinum dish with 5 ml. of nitric acid, 2 ml. of sulfuric acid, and 10 ml. of hydrofluoric acid. Evaporate carefully to complete dryness. Take up the residue with 5 ml. of 1 : 1 perchloric acid, and transfer to a 50-ml. Nessler tube. If the solution is cloudy and does not settle readily it may be filtered through a small paper, the blank being similarly treated.

Add 5 ml. of hydrochloric acid, 2 ml. of 3 per cent H_2O_2 , 5 ml. of 10 per cent potassium thiocyanate, and dilute to the mark. Run the standard iron solution from a buret into two other tubes containing the same amounts of hydrochloric acid, hydrogen peroxide, potassium thiocyanate, and water, until the colors match those of the sample and blank.

Deduct the amount of standard iron solution used for the blank from that used for the sample, and calculate the percentage of iron.

The standard iron solution is prepared by dissolving 0.1 gram of pure iron wire in 10 ml. of iron-free hydrochloric acid, adding 5 ml. of 1 : 1 perchloric acid, and diluting to 1 liter in a volumetric flask. One milliliter contains 0.0001 gram iron.

LEAD MINERALS

Mineral Name	Chemical Formula	% Pb	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Galena.....	PbS	86.6	Lead-gray, metallic luster	7.5	Au, Ag, Cu, Zn, Fe, As, Sb, Bi, Cd, Ca, P, V	HCl, HNO ₃	
Cerussite.....	PbCO ₃	77.7	White or tinted	6.5	Au, Ag, Cu, Zn, Fe, As, Sb, Bi, Cd, Ca, P, V	HCl, HNO ₃	
Anglesite.....	PbSO ₄	73.6	White or tinted	6.3	Same	HCl (Difficultly)	Na ₂ CO ₃ , Na ₂ O ₂
Pyromorphite.....	3 Pb ₃ P ₂ O ₈ ·PbCl ₂	76.4	White to yellowish	6.5	Same	HNO ₃	
Mimetite.....	3 Pb ₃ As ₂ O ₈ ·PbCl ₂	69.7	White to yellowish	7.0	Same	HNO ₃	
Wulfenite.....	PbMoO ₄	56.5	White to yellowish	7.0	Ca, Zn, Fe, W, V	HCl+H ₂ SO ₄	
Vanadinite.....	3 Pb ₃ V ₂ O ₈ ·PbCl ₂	73.2	White to yellowish	7.0	Zn, Cu, Mo, P, As	HCl, HNO ₃	

Lead is most frequently combined with copper, bismuth, arsenic, antimony, or silver, in minerals; less frequently with chromium, selenium, tellurium, tin, and uranium. Decomposition is usually effected by acids. Refractory materials and silicates are satisfactorily broken up by alkaline fusion after a preliminary acid treatment. The sulfide minerals, in powdered form, are all gray to black with metallic luster, while the oxide, chromate, and vanadate minerals are commonly yellow to orange in color.

CHAPTER XVI

LEAD

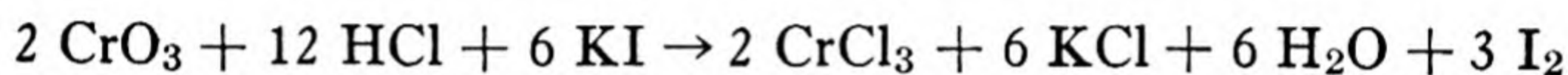
I. CHROMATE METHOD

A. Application

In this method the lead is eventually precipitated as chromate, PbCrO_4 . This is then decomposed by hydrochloric acid, as follows:

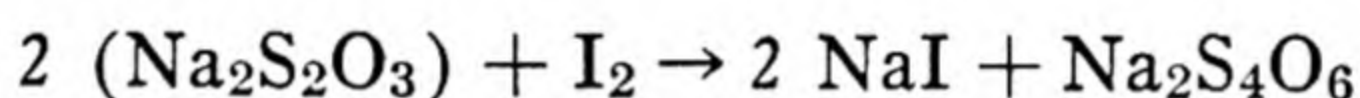


Potassium iodide is now added, which the chromic acid decomposes with the liberation of iodine, according to the reaction



The iodine is titrated with thiosulfate.

The above reactions show that $\text{Pb} = \text{CrO}_3$, as $2 \text{CrO}_3 = 3 \text{I}_2$ then $2 \text{Pb} = 3 \text{I}_2$. In the titration, the reaction between the thiosulfate and iodine is



The method is applicable to a large variety of ores and metallurgical products.

B. Interfering Elements

All the barium and more or less of other elements such as molybdenum, tungsten, thallium, silver, iron, and manganese may contaminate the lead sulfate precipitate if present in large amounts. Silver, bismuth, barium, mercury, thallium, and tin form precipitates with potassium dichromate. Silver is best removed as the chloride before taking the sample to fumes with sulfuric acid. Mercury and thallium do not interfere if kept in their higher valences. Tin, nickel, and chromium may contaminate the lead sulfate precipitate under certain conditions.

Bismuth in small amount does not interfere. With several per cent present, some may remain as basic sulfate with the lead sulfate and produce high results. If bismuth is suspected it may be re-

moved, just before the lead chromate is filtered, by adding about 2 grams of citric acid dissolved in a little hot water. Any bismuth chromate will go into solution at once. Filter without delay.

C. Procedure

Prepare the following solutions:

Extraction Solution. Make a cold saturated solution of commercial sodium acetate in distilled water and filter it. Mix 1 volume with $1\frac{1}{2}$ volumes of distilled water, and add to the mixture 25 ml. of glacial acetic acid per liter. Use nearly boiling in a wash bottle.

Hydrochloric Acid Mixture. Make a cold saturated solution of table salt in distilled water and filter it. To 1 liter of the filtrate add 150 ml. of distilled water and 100 ml. of strong hydrochloric acid. Use cold in a wash bottle.

Potassium Dichromate. A cold saturated solution of the powdered commercial salt in distilled water. Filter, or allow to settle.

a. Weigh 0.5 gram of the ore into a 250-ml. beaker. It is usually best to begin the treatment with 20 ml. of strong hydrochloric acid and heat gently until all iron oxide, etc., is in solution. This treatment will also decompose galena and expel the hydrogen sulfide. If sulfides remain that resist hydrochloric acid, add 5 ml. of strong nitric acid and continue the heating. Finally, if necessary, add 5-10 ml. more hydrochloric acid and again heat, to bring all the lead chloride into solution.

Decomposition and solution having been satisfactorily effected, add 5 ml. of strong sulfuric acid and boil, finally, over a free flame, until the white fumes are coming off copiously. Cool, add about 30 ml. of water, and heat to boiling. Allow to stand, hot, until the anhydrous ferric sulfate usually present has dissolved. Now add 10 ml. of alcohol (either grain or wood), and then cool to room temperature, or cooler, and filter through a 9-cm. filter. (The alcohol is not absolutely essential except for the low percentages, say below 10 per cent lead.) Wash the precipitate with cold dilute (1 : 10) sulfuric acid at least four times. Give the beaker a final rinse with cold water.

b. *Decomposition of Refractory Material.* Metallurgical products, such as antimonial slags, may obstinately resist the ordinary methods of attack. For these try the following plans, first (1), and

then, if that fails, try (2). The second is more troublesome but will probably succeed almost always.

(1) Treat 0.5 gram of the finely ground material precisely as described in **Antimony, I, C, a**. With oxidized material the piece of filter paper is very essential. It causes a reduction of antimony to the *ous* condition and thus promotes its solution. In the presence of much sulfur or carbon the paper is unnecessary. To the cool melt add 5 ml. of sulfuric acid, 10 ml. of water, and 5 ml. of hydrochloric acid. Boil to strong fumes. Cool, add 30 ml. of water, heat to boiling, and then maintain hot, but not boiling, with occasional agitation, until all the soluble salts, including any anhydrous ferric sulfate, are dissolved. Add 10 ml. of alcohol, cool under the tap, filter and wash the lead sulfate as usual, and proceed with it according to the method selected. If the permanganate method is to be employed, dilute with 100 ml. of water instead of 30 ml.

(2) Employ the peroxide fusion, as described for chrome iron or (**Chromium, I, C, a**). If sulfide or carbon is present, modify the method by the addition of sodium carbonate to prevent too violent action, as described in **Molybdenum, II, C, a**. In either case proceed to the point where the crucible has been removed from the solution of the melt. Cover the casserole, and boil to a bulk of 100 ml. or less. Now transfer the mixture to a 250-ml. beaker, retaining any scales of iron oxide in the casserole, cleansing them by several slight additions of water and decanting. Cool the mixture in the beaker, acidify slightly with sulfuric acid (avoiding loss by effervescence), and then add 5 ml. in excess and 10 ml. of alcohol. Cool under the tap, filter off the lead sulfate, and treat it as usual.

c. Now open the filter, from **a** or **b**, carefully, and spread it in the funnel. Wash the precipitate from it into the beaker again with a jet of hot water, using as little as possible. Have about 25 ml. of extraction solution in a small beaker. Drop the filter into this and heat to boiling. Stir the paper about in the hot liquid so as to shred it as much as possible. This is to dissolve every trace of lead sulfate still adhering to the filter. Moisten a small wad of absorbent cotton placed in the apex of the funnel, and pour the mixture through it into the beaker containing the lead sulfate, rinsing with hot water. Now, continue to wash the cotton with

hot water, but do not allow the filtrate to reach a greater volume than about 150 ml. When the liquid is heated at this stage any separated or undissolved lead sulfate (except as below) will go into solution.

d. The procedure described in c nearly always suffices, but when barium is present some of the lead sulfate may fail to dissolve; therefore, when barium is known to be present, or in case of doubt, proceed as follows: Without removing the filter, rinse the lead sulfate back into the beaker with a jet of hot water, using as little as possible. Lift the fold of the filter to catch any deposit underneath. Add 10 ml. of hydrochloric acid to the mixture in the beaker, and then boil to pastiness, almost dryness. Now add about 25 ml. of extraction solution and boil. Continue to add extraction solution, while boiling, until all the lead sulfate has dissolved, avoiding unnecessary excess. Filter through the last filter into a 250-ml. beaker and wash with hot water until the filtrate has reached a volume of about 150 ml. It is a good plan to have a similar beaker, with a mark on it for comparison, so as always to obtain, approximately, the right volume.

e. Having obtained a solution of the lead sulfate, by procedure c or d, dilute, if necessary, to a volume of approximately 150 ml. with hot water, and heat to boiling. Add to the boiling solution, preferably with a pipet, 10 ml. of the prepared potassium dichromate solution. Boil the mixture very gently for about seven minutes. This is necessary to insure a fixed constitution for the lead chromate, which is not quite normal. Longer boiling does no harm. Now filter through an 11-cm. filter. Wash out the beaker with hot water, and then wash the filter and precipitate ten times with a hot dilute solution of sodium acetate (50 ml. of a cold saturated solution of the commercial salt diluted to 1 liter), using about 5-6 ml. each time. Now place a clean flask under the funnel, and, with a jet of cold hydrochloric acid mixture, stir up and dissolve the precipitate on the filter, and continue washing with the same mixture until all the residue and every trace of color are removed from the filter. Use at least 50 ml. of the mixture, in order that the subsequent reactions may have the proper conditions. Wash the filter finally with cold water, or at once dilute the filtrate until the flask is half full. Either one of two procedures is now to be followed, according to the amount of lead apparently present.

f. *With Not Over 20 Per Cent Lead.* Add 2 ml. of a 50 per cent solution of potassium iodide, mix and titrate at once (to avoid possible loss of iodine by volatilization) with a standard sodium thiosulfate solution until the brown color becomes faint; then add sufficient starch solution to produce a strong blue color, and finish the titration very slowly, finally drop by drop, until the solution becomes a clear pale green with no tinge of blue. The end point is very sharp, and care must be exercised or it may easily be passed. It is best to have a white surface under the flask.

g. *With Over 20 Per Cent Lead.* Pour all but about 25 ml. of the liquid in the flask into a beaker. To the solution still remaining, add about 25 ml. of the hydrochloric acid mixture and 2 ml. of the above potassium iodide solution. Mix and titrate at once with the standard thiosulfate until the brown color has become faint. Now add a portion of the solution reserved in the beaker and again titrate to a faint brown color. Continue thus until the last of the reserved solution has been rinsed into the flask; then finish the titration as in f. In pouring from the beaker it is best to use a glass rod, so as to avoid having to wash the lip each time and unnecessarily increasing the volume of liquid in the flask, which otherwise may become inconveniently full.

The thiosulfate solution used in the iodide copper method is satisfactory for lead, but should be standardized against pure lead. The copper value of thiosulfate, multiplied by 1.087, will give a close approximation to the lead value. See Chapter XXXIII.

h. *Notes.* The final solution is not a very good solvent for iodine, and therefore, if much is liberated at once, there is danger of loss by volatilization. To avoid this, the procedure described in g for the higher percentages of lead has been found the best.

The amount of potassium iodide prescribed is much more than theoretically required, but it is never safe to use less, as the reactions are then likely to proceed too slowly.

Testing the completeness of the extraction is rarely necessary, as the solution of all the lead sulfate is usually easily seen.

Prepare only a wash bottleful of the dilute sodium acetate wash at a time, as, unless the solution is heated frequently, a fungus growth develops that will clog the filter.

If the end point is passed in titrating, it may be "brought back" with a dilute solution of potassium dichromate or permanganate, of

which the comparative value need not be known. Simply run in from a buret a measured number of drops until the blue color returns; titrate once more, and take reading. Now again run in the same number of drops of the correction solution as before and again finish the thiosulfate titration and read the buret. Subtract the difference between the two readings from the first one to obtain the true end point for the lead.

If, in titrating by portions, as in g, the end point is slightly passed with any of the portions, no appreciable error will be introduced if more of the reserved solution is quickly added, as the thiosulfate solution is decomposed only very slowly by the acid mixture.

The constitution of the lead chromate is a vital point. It depends upon the various conditions of heat, acidity, etc. By operating as described, differences in constitution are minimized and a slightly acid chromate of practically constant composition is obtained. The normal chromate, under the conditions obtaining, is difficult to maintain as such.

II. MOLYBDATE METHOD¹

A. Application

Alexander's method, or some modification of it, is the one most commonly employed in western smelting works. The principal objection to it is the difficulty of accurately determining very low percentages of lead, on account of the slowness of the reaction. Alexander's original method did not sufficiently provide for the presence of calcium, which is a frequent constituent of lead ores. It was partly to avoid this source of error that the method was modified as below. Calcium forms a molybdate which is more or less insoluble under the conditions of the titration and tends to raise the results in a rather irregular manner.

B. Interfering Elements

Besides the alkaline earths, which form insoluble sulfates, silver may occasionally be present in sufficient quantity to cause trouble. The lead sulfate precipitate will frequently retain iron that cannot be dissolved or washed out, but which finally goes into solution with the lead sulfate and gives a color with tannic acid on the test plate.

¹ H. Alexander, *Eng. Min. J.*, 55, 1, 1893.

Large amounts of insoluble material tend to hinder the precipitation of the lead molybdate and obscure the end point. Excessive amounts of ammonium acetate should be avoided.

C. Procedure

a. Decompose an appropriate weight of the sample with nitric acid and potassium chlorate. Evaporate just to dryness, and take up the residue in 10 ml. hydrochloric acid. Dilute with a little water, heat to boiling, and, when all the lead chloride is in solution as well as other soluble salts, filter off the insoluble residue, receiving the filtrate in a 250-ml. beaker. Wash well with hot 1 : 1 hydrochloric acid and hot water. Any other convenient method of decomposition may be used, the lead ultimately being obtained in a clear hydrochloric acid solution.

b. Neutralize the filtrate with ammonium hydroxide until a precipitate starts to form. Dilute to 100 ml., and pass in hydrogen sulfide gas until the lead is completely precipitated as sulfide. Filter on a close paper and wash with a H_2S wash solution. Put the paper and sulfide precipitate back in the beaker, cover, add 5 ml. of sulfuric acid and 10 ml. of nitric acid through the lip of the beaker, and place on the hot plate. Take to fumes, adding small additional amounts of nitric acid till all the carbon is burnt off, then finally fuming strongly.

c. Cool, add about 30 ml. of water, and heat to boiling. Add 10 ml. of alcohol, cool to room temperature, and filter on a close paper. Wash with 10 per cent sulfuric acid and finally with cold water. Transfer the paper and precipitate of lead sulfate back to the beaker, add 10 to 20 ml., according to the amount of lead present, of ammonium acetate solution (250 ml. of a saturated solution of ammonium acetate and 150 ml. of acetic acid per liter), and heat to boiling. Dilute to 200 ml. with hot water, and titrate with the standard ammonium molybdate solution (see **Chapter XXXIII**) as follows:

Pour about two-thirds of the hot lead solution into another beaker, and run the molybdate solution into it from a buret until a drop from the beaker, when placed on a glazed porcelain plate and touched with a drop of a solution of tannic acid (about 0.1 gram dissolved in 20 ml. of water), gives a brown or yellow tinge. Now

add more of the lead solution from the beaker, and continue the titration until the end point is again passed. Continue thus to approach the true end point, observing greater caution each time. Finally, when only a few milliliters remain in the first beaker, pour the entire mixture in the second beaker into the first and then back into the second beaker, and finish the titration 2 drops at a time. When the final yellow tinge is obtained, some of the immediately preceding tests may have developed a tinge also. From the readings of the buret deduct the volume of 2 drops for each test thus showing a color. Multiply the corrected reading by the percentage value of 1 ml. of the molybdate solution in lead to obtain the percentage of lead in the ore.

D. Modification

When calcium is known to be absent or present only in small amount, the above process may be shortened as follows:

Decompose the sample as in I, C, a, until the washed lead sulfate precipitate is obtained on the filter, and proceed as above.

III. PERMANGANATE METHOD

A. Application

This is a very satisfactory method in the absence of large amounts of calcium. As much as 10 per cent of CaO , however, does not interfere, as this amount of CaO , as sulfate, is soluble in the 100 ml. of acid liquid from which the lead sulfate is filtered. Larger amounts of CaO could undoubtedly be provided for by still greater dilution at this point, without serious effect in dissolving lead sulfate. Barium sulfate is not greatly affected by the chemical transformations, and what goes through to the end is sufficiently soluble, as oxalate, to remain in solution. At the outset, however, barium and lead form more or less of a double sulfate, in which the lead fails to be completely converted to carbonate. This would produce low results, were it not for the hydrochloric acid treatment of the sulfates, described below, which breaks up the compound.

B. Procedure

a. Decompose 0.5 gram of the ore in a 250-ml. beaker as described in previous methods. Decomposition having been effected,

add 6 ml. of sulfuric acid and boil to strong fumes. Allow to cool, add 100 ml. of cold water, and heat to boiling. Remove from the heat, add 10 ml. of alcohol (grain or wood), cautiously, and cool under the tap. Fold a 9-cm. filter, taking particular care to crease the fold that will come next to the precipitate as thin as possible, so that it will lie flat and not easily allow material to get under the edge. Filter the cold mixture through this, returning the first portions of the filtrate if not clear. Wash six times with cold water containing 10 per cent of alcohol. Any traces of lead sulfate remaining in the beaker will be recovered subsequently.

b. With a jet of hot water, using as little as possible, rinse the precipitate from the filter, through a short funnel, back into the beaker. (In the known or assumed presence of barium, interpolate the following short procedure: Add 10 ml. of strong hydrochloric acid and boil over a free flame nearly to dryness. Allow to cool; add 20 ml. of water and a few drops of ammonia, sufficient to neutralize the acid.) Place the beaker again under the original funnel and pour through the filter 10 ml. of a cold saturated solution of ammonium carbonate. Remove the beaker and heat the contents just to boiling, then cool completely under the tap. Pour the cold mixture through the original filter. The filtrate is to be rejected. Wash out the beaker well with cold water, pouring through the filter, and then wash filter and precipitate ten times with cold water containing about 5 per cent of the ammonium carbonate solution.

c. Again using a jet of hot water, wash the precipitate from the filter into a small beaker. Add 5-6 ml. of glacial acetic acid and 2 or 3 drops of ammonia, and heat to boiling. Replace the original beaker under the funnel, and pour the hot acid mixture through the filter. Wash out the beaker with hot water, and then wash the filter ten times with hot water slightly acidulated with acetic acid.

d. Add to the filtrate 10 ml. of a cold saturated solution of oxalic acid, heat to boiling, and then cool completely, under the tap. Be particular to get as cold as possible. Now filter the lead oxalate through a 9-cm. filter. Using cold water, wash out the beaker thoroughly, and then wash filter and precipitate ten times.

e. Place about 25 ml. of cold water in the beaker; add 5-6 ml. of sulfuric acid and then about 100 ml. of hot water. Drop in the filter and precipitate. Wipe out any lead oxalate adhering in the

funnel with a small piece of filter paper and drop into the beaker. Heat the acid mixture nearly to boiling and then titrate it with standard potassium permanganate solution to a faint pink tinge. Calculate the result from the known lead value of the permanganate.

The permanganate used for iron titrations will serve, although rather strong for lead. Theoretically, 1.854 times the Fe factor will give the Pb factor. Owing to slight losses of lead in the process an empirical factor must be used. This is 1.861 times the Fe factor. On the basis of this factor an 0.5 gram of ore taken for assay, 1 ml. of a permanganate solution containing 1.524 grams per liter will equal 1 per cent lead.

IV. FERROCYANIDE METHOD

A. Application

This method gives good results and may serve as a check method against any of the preceding.

B. Interfering Elements

While the method answers ordinarily, in order to provide against bismuth and antimony (the basic sulfates of which might cause trouble), the following modification may be adopted: To the sufficiently cool residue of the sulfuric acid evaporation add 10 ml. of dilute sulfuric acid (1 : 10) and about 2 grams of Rochelle salt. When this has dissolved, add 40 ml. of water, heat to boiling, and proceed as usual.

Calcium does not interfere with this method except by the slight solvent action exercised by calcium acetate on the brown uranium acetate of the test. Thirty per cent of CaO in an ore, however, occasions no serious trouble. Calcium sulfate must not be allowed in the acetate solution, as it might occasion a loss of lead by precipitation as sulfate.

C. Procedure

It is better to start with 1 gram, rather than 0.5 gram of the ore. Decompose precisely as described for the chromate method (I, C, a). Continue as there directed until the washed mixture of lead sulfate and gangue is obtained on the filter. The last two washings should be with pure water, to remove most of the acid. See that

the filter is well creased, so as to lie as flat as possible and prevent solid matter from getting under the fold. Rinse the contents of the filter (without removing it from its funnel) into the original beaker as completely as possible with cold water. Not more than 50 ml. of water need be used. Add 10 ml. of a cold saturated solution of commercial ammonium carbonate, pouring it through the original filter, and heat the mixture to boiling. The heating is necessary to insure the complete conversion of any possible calcium sulfate to carbonate. Cool to ordinary temperature, under the tap or otherwise, and filter through the original filter, washing beaker and precipitate thoroughly with cold water. Place in the beaker some dilute acetic acid, equivalent to a mixture of about 5 ml. of the glacial acid and 25 ml. of water, and have it heating while the filter is being washed. The beaker usually contains a small residue of lead carbonate which is thus recovered. Place the filter and contents in a large beaker and add the boiling hot acetic acid. Stir the mixture about until the carbonates are entirely dissolved, heating if necessary. Dilute with about 100 ml. of cold water, and the solution is ready for titration with standard potassium ferrocyanide solution. The end point is indicated by the usual brown tinge when a drop is tested on a porcelain plate with a drop of a saturated solution of uranium acetate. Reserve a portion of the solution, and titrate the main body rapidly until the end point is passed; then add most of the reserved portion and titrate with more caution until the end point is once more passed. Finally rinse in the balance of the reserve and finish the titration 2 drops at a time, stirring well after each addition. When the final brown tinge is thus obtained, allow a little time for the immediately previous tests to develop, and then deduct from the buret reading an amount equal to 2 more drops than are indicated by the tests, as a solution containing no lead shows the test only after the addition of the third drop of ferrocyanide.

See Chapter XXXIII for the preparation and standardization of the ferrocyanide solution.

MAGNESIUM MINERALS

Mineral Name	Chemical Formula	% MgO	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Magnesite...	MgCO ₃	47.6	White or tinted	3.0	Fe, Mn, Ca, Na, K, Si	HCl	
Brucite.....	Mg(OH) ₂	69.0	White or tinted, alkaline reaction in water	2.4	Fe, Mn, Ca, Na, K, Si	HCl	
Dolomite....	CaCO ₃ ·MgCO ₃	21.7	White or tinted	2.8	All common elements	HCl	
Talc.....	3 MgO·4 SiO ₂ ·H ₂ O	31.7	White to green, soapy feel	2.7	Fe, Mn, Ca, Ni	Insoluble	Na ₂ CO ₃
Chrysotile...	3 MgO·2 SiO ₂ ·2 H ₂ O	43.0	White to greenish, waxy luster and feel	2.2	Fe, Ni, Cr, Ca, Mn	HCl, H ₂ SO ₄	Na ₂ CO ₃
Amphiboles..	R SiO ₃ R = CaMgFeMnNa ₂ K ₂ H ₂	Variable	Gray to greenish or brownish	2.9 to 3.6	Al, Ti	Insoluble	Na ₂ CO ₃
Spinel.....	MgO·Al ₂ O ₃	28.2	White or tinted	4.0	Ca, Si, Fe, Mn, Cr	H ₂ SO ₄ (difficultly)	KHSO ₄ , Na ₂ CO ₃
Epsomite....	MgSO ₄ ·7H ₂ O	16.3	White	1.7	Fe, Mn, Ca, Na, K	Water soluble	

Magnesium is a common constituent of gangue minerals, more or less of the magnesium going into solution in acid decompositions. All the silicates yield readily to alkali carbonate fusion. A few of the spinels, however, are difficultly decomposed by carbonate fusion but may be broken up with sodium peroxide.

CHAPTER XVII

MAGNESIUM

I. PHOSPHATE METHOD

A. Application

The determination of magnesium by precipitation as magnesium ammonium phosphate, though not so rapid a technical method as could be desired, is still the most reliable and accurate procedure for the complex materials encountered in metallurgical analysis. A great deal of work has been done by various investigators regarding the conditions necessary for correct precipitation and ignition of magnesium ammonium phosphate. For a complete discussion of the subject, see the works of Gooch and Austin,¹ Epperson,² and Lundell and Hoffman.³

B. Interfering Elements

None of the common elements, except phosphorus, arsenic, and barium, interfere seriously with the determination of magnesium, provided that the regular separations for the hydrogen sulfide and ammonium sulfide groups have been made. Incomplete separations, due to improper treatment or to the presence of elements such as fluorine or carbon, will leave elements present which very likely will precipitate as phosphates.

Barium is best removed as the sulfate prior to the separation by hydrogen sulfide. Phosphorus or arsenic, present in more than small amounts, will cause low results.

C. Procedure

a. Treat an appropriate weight of the sample as described under Calcium I, C, a, b, c, and d.

¹ F. A. Gooch and M. Austin, *Chem. News.*, 79, 255, 1899.

² A. W. Epperson, *J. Am. Chem. Soc.*, 50, 321, 1928.

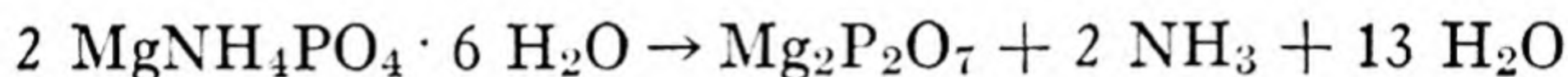
³ J. I. Hoffman and G. E. F. Lundell, *Bur. Standards J. Research*, 5, 279, 1930.

b. Evaporate the filtrate from the oxalate precipitations, if necessary, to a volume of 200 ml., and make acid with hydrochloric acid, adding about 4 or 5 ml. in excess. If excessive amounts of ammonium chloride or ammonium oxalate have accumulated, concentrate the filtrate from the calcium oxalate to small bulk by boiling in a large porcelain casserole, and when salts show a tendency to separate, transfer to a platinum dish or smaller porcelain casserole, in separate small portions if necessary, and evaporate on the water bath to complete dryness. When dry, ignite gently to expel the ammonium salts. Cool, dissolve the residue in 5 ml. hydrochloric acid, dilute to 100 ml., and filter if necessary.

c. Add 0.5 gram of solid ammonium phosphate (dibasic), or 5 ml. of a 10 per cent solution, for each 10 mg. of magnesium present. Put a crushed ice cube in the solution or cool under the tap, then add ammonium hydroxide from a dispensing buret, while stirring constantly, until the ammonia is in about 10 per cent excess, that is, 20 ml. for 200 ml. of solution. Stir vigorously for at least five minutes, and allow the cold solution to stand for four hours or preferably overnight. The precipitation may be hastened by continuous agitation with an electric mixer; one hour will suffice for technical work. Decant the supernatant solution through a close 9-cm. ashless filter, transfer the precipitate from the beaker to the paper with 2 per cent ammonia, and wash several times with the same solution.

Dissolve any precipitate adhering to the wall of the beaker with 20 ml. of 1 : 4 hydrochloric acid, and set the beaker and acid on the plate to warm. Place a clean 150-ml. beaker under the funnel containing the bulk of the phosphate precipitate. Now dissolve the precipitate through the paper with the warm acid solution, wash with dilute hydrochloric acid, then water, and finally with 2 per cent ammonia. To the solution, in the 150-ml. beaker, add a few drops of ammonium phosphate solution and some crushed ice, and then reprecipitate the magnesium with ammonia as before. Let stand for two hours with occasional stirring during the first hour. Filter through the same paper as before, and wash well with the 2 per cent ammonia wash solution. The beaker must be scrubbed thoroughly with a rubber policeman to make sure that none is retained on the bottom or side walls.

d. Remove the excess moisture from the paper, and precipitate by means of an aspirator and suction flask. Take the paper from the funnel and fold it so that all the paper except one thickness is on the top of the precipitate. Flatten between the thumb and forefinger, taking care not to break the paper, and place in a No. 00 porcelain crucible (preferably with black glaze on the inside) so that the flattened wad is hung up on the side walls of the crucible about halfway down, the bulk of the paper being on top. Place the crucible in a cold muffle, and bring the temperature slowly to about 1000° C. The paper should not be allowed to burn with an open flame. When the contents of the crucible are pure white, remove the crucible from the muffle and cool in a desiccator.

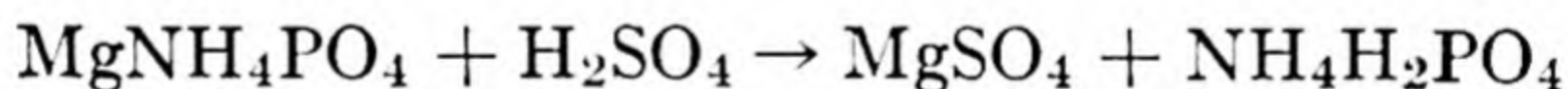


Transfer the ignited precipitate to the balance pan, and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$. This weight multiplied by 0.2184 will give that of the Mg, or multiplied by 0.3621, that of the MgO.

II. VOLUMETRIC METHOD ⁴

A. Application

This is a modification of Stolba's method in which the precipitated magnesium ammonium phosphate is titrated with standard sulfuric acid, the reaction being:



A measured excess of sulfuric acid is used and titrated back with standard sodium hydroxide. The results obtained are very satisfactory for routine technical analyses.

B. Procedure

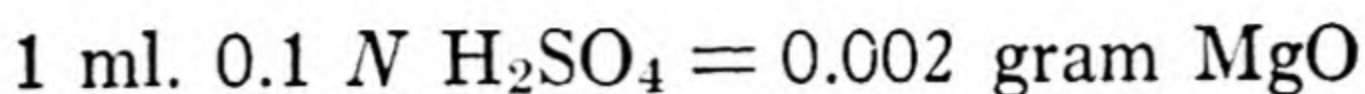
The ore or other material is treated by the usual methods, and the filtrate from the calcium oxalate precipitation is then treated as follows:

Add ammonia (sp. gr. 0.90) equivalent to one-tenth of the solution. Cool in water to 20° to 25° C. Precipitate by adding

⁴ J. O. Handy, *J. Am. Chem. Soc.*, **22**, 31, 1900.

slowly (with constant stirring) a saturated solution of sodium ammonium phosphate, using 1 ml. for each 0.01 gram magnesium oxide. Stir vigorously for five minutes or shake in a flask for an equal length of time. If the solution is stirred, let it stand until the clarification of the upper liquid shows that the reaction is complete. In flask precipitations, if more than 0.002 gram of magnesium oxide is present the solution may be filtered in fifteen minutes. Suction may be used if desired, but if many solutions are to be filtered at once little is gained thereby. Use 10 per cent ammonia wash (1 part ammonia [sp. gr. 0.90] to 9 of water). Deliver it preferably from an aspirator bottle placed about 4 feet above the bench. Wash by decantation as far as possible. Finally, wash the precipitate which has gone on the filter back into the beaker, stir it up with the ammonia wash, and bring it again completely on the filter paper. Wash once more, leaving the upper edge of the filter clear of precipitate so that it can be handled. Avoid assembling all the precipitate in the apex, but leave it fairly evenly distributed over the lower two-thirds of the paper. Allow the precipitates to drain, and then transfer each in turn to a dry 5-inch filter paper, allowing them to remain there, open and face upward, until the bulk of the moisture has been absorbed. After about three minutes transfer them to fresh dry filters, and if the precipitate is heavy to a third set a few minutes later. Then place the filters on a shelf to dry at the temperature of the room, or place filter papers and backing on the grating of an air oven having a temperature of 50° to 60° C. After fifteen or twenty minutes in the oven, or forty-five minutes in the air, watch for the time when the filters have dried inward half an inch from the margin. This has been found to indicate that the evaporation has gone far enough to insure the expulsion of the free ammonia. Now place the precipitates and filters in small dry beakers, and treat each with a measured excess of decinormal sulfuric acid, stirring until the papers are disintegrated and the precipitates dissolved. Then add 2 drops of a 0.1 per cent alcoholic solution of methyl orange. If this gives a clear decided pink, enough acid has been added. If it is only faintly pink, the excess of acid is slight and some minute particles may have escaped solution. In such cases add 5 ml. more decinormal sulfuric acid and stir well. Finally, dilute to about 100 ml. and titrate back with deci-

normal sodium hydroxide solution to the appearance of a clear yellow color, free from all suggestion of pink.



If the filtrations have taken place during the latter part of the day, the filters may be removed from the funnels and allowed to stand overnight, after which they are titrated as described.

Notes on the above Method (Handy). If the drying of the precipitate proceeds too far, solution in decinormal sulfuric acid is slow. If, however, the drying is stopped at the point described, there is enough moisture left so that, on stirring, the precipitate blends quickly with the acid and soon dissolves.

The tendency of magnesium to precipitate with iron and aluminum and with calcium oxalate must be met by re-solution in hydrochloric acid and reprecipitation. When the amount of calcium is considerable it is best to burn off the first oxalate precipitate before dissolving in hydrochloric acid. By this means the oxalate is decomposed and the addition of ammonia alone does not cause its sudden reprecipitation. Even in the second precipitation, if the boiling is allowed to proceed longer than is necessary to make the finely crystalline calcium oxalate settle well, some magnesium oxalate is sure to precipitate, betraying its presence by its coarser texture. The solution for magnesium precipitation usually does and always should contain in the form of ammonium chloride the equivalent of 5 ml. of concentrated hydrochloric acid per 100 ml.

III. 8-HYDROXYQUINOLINE METHOD⁵

A. Application

As 8-hydroxyquinoline precipitates a great number of elements, its use offers no advantages over the phosphate method when handling complex material. The following method, however, is extremely rapid, and finds use in routine analyses for materials containing relatively few interfering elements, such as limestone, dolomite, magnesium ores, and cement. The procedure is best applied

⁵ R. Berg, *Z. anal. Chem.*, 71, 23, 1927; F. L. Hahn, *Z. anal. Chem.*, 86, 153, 1931; J. C. Redmond and H. A. Bright, *Nat. Bur. Standards J. Research*, 6, 113, 1931. For an excellent bibliography on this reagent, see *Organic Reagents for Metals*, 3d ed., published by Hopkin and Williams, Ltd., London, 1938.

to lower-grade products, owing to the bulk of the quinolate precipitate.

B. Interfering Elements

Elements such as Sb, Bi, Cd, Cu, Pb, Hg, Ag, and Sn are best removed by precipitation with hydrogen sulfide in acid solution. Al, Be, Fe, Ti, Zr, Th, and the rare earths are eliminated in the ordinary procedure in the R_2O_3 precipitate. Co, Ni, Mn, Zn, quadrivalent vanadium, and sexivalent uranium may be removed along with the preceding elements by means of ammonium sulfide. Interference by calcium or strontium is avoided in the volumetric method by precipitation as the corresponding oxalates.

C. Procedure

The following directions are those given for the determination of magnesium in Portland cement developed by the National Bureau of Standards.⁶

a. To a 0.5-gram sample in a 400-ml. beaker add 10 ml. of water and 10 ml. of hydrochloric acid (sp. gr. 1.18). Heat gently and grind any coarse particles with the flattened end of a glass rod until decomposition is complete. Dilute to 150 ml. with hot water.

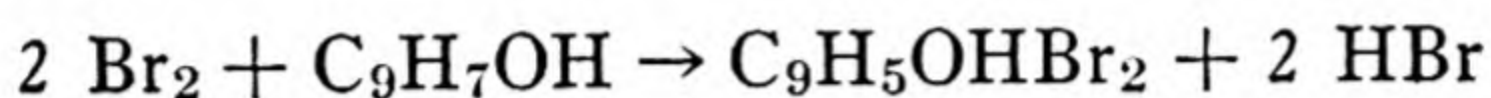
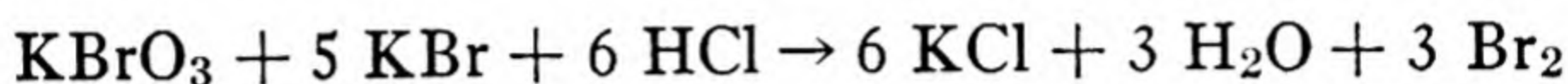
To the solution add 3 drops of methyl red (0.02 per cent alcoholic solution) and then ammonium hydroxide (sp. gr. 0.90) until the solution is distinctly yellow. Add macerated filter paper, and heat to boiling. Boil from one to two minutes, remove from the hot plate, and allow to stand until the precipitate has settled. Filter without delay, and wash the precipitate with a hot 2 per cent solution of ammonium chloride. To the filtrate add 1 ml. of ammonium hydroxide, and heat to boiling. When boiling, add 25 ml. of a hot 4 per cent solution of ammonium oxalate and continue boiling for two minutes. Digest on the steam bath for ten to fifteen minutes.

b. Cool the solution to 70° C., add sufficient 8-hydroxyquinoline solution (25 grams of the reagent dissolved in 60 ml. of glacial acetic acid and diluted to 2 liters with water)⁷ to precipitate all the magnesium, and then 4 ml. of ammonium hydroxide per 100 ml. of solution. Stir on a mechanical stirring machine for fifteen min-

⁶ *Nat. Bur. Standards J. Research*, 10, 826, 1933, by permission of Dr. G. E. F. Lundell.

⁷ One milliliter of this solution is equivalent to 0.0016 gram MgO.

utes, and set aside until the precipitate has settled. Filter and wash with hot dilute ammonium hydroxide (1 : 40). Dissolve the precipitate in 50 to 75 ml. of hot dilute hydrochloric acid (1 : 9), dilute the resulting solution to 200 ml., and add 15 ml. of concentrated hydrochloric acid. Cool to 25° C., and add a measured amount of 0.2 *N* standard bromate-bromide solution in moderate excess, as determined by testing with potassium iodide-starch paper after stirring and letting stand for 30 seconds.



The excess bromine liberated after complete bromination of the 8-hydroxyquinoline in solution reacts with the potassium iodide next added to liberate free iodine.

c. Add 10 ml. of 25 per cent potassium iodide solution, stir well, and then titrate with standard 0.1 *N* sodium thiosulfate solution until the color becomes a pale brownish yellow. Add 2 ml. of starch solution and finish the titration to the disappearance of the blue color.

The number of milliliters of thiosulfate used, deducted from the number of milliliters of thiosulfate necessary to titrate all the standard bromate-bromide solution added, gives the milliliters of thiosulfate solution equivalent to the magnesium present. One milliliter of exactly 0.1 *N* thiosulfate is equal to 0.000504 gram of MgO.

Consult **Chapter XXXIII** for the preparation and standardization of solutions.

MANGANESE MINERALS

Mineral Name	Chemical Formula	% Mn	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Pyrolusite.....	MnO ₂	63.2	Black, sooty	4.8	Fe, Ba, Ca, Mg, Si, Al, Na, K, Zn, Co, Ag, CO ₂	HCl	Na ₂ CO ₃
Psilomelane.....	MnO ₂ · nH ₂ O	Variable	Brownish to black, shining	3.3-4.7	Same as above	HCl	Na ₂ CO ₃
Manganite.....	Mn ₂ O ₃ · H ₂ O	62.4	Reddish brown to black	4.3	Same as above	HCl	Na ₂ CO ₃
Braunite.....	3 Mn ₂ O ₃ · MnSiO ₃	63.6	Dark brownish black to gray	4.8	Same as above	HCl	Na ₂ CO ₃
Rhodochrosite.....	MnCO ₃	47.8	White or tinted red to brown	3.5	Same as above	HCl	Na ₂ CO ₃

Manganese, like iron, is nearly always found in the analyses of ores, minerals, and rocks, often only as a trace, but practically always present. As a result of its widespread occurrence, it is often a nuisance to the analyst and very commonly is the cause for errors in the determinations of such elements as aluminum, beryllium, calcium, and magnesium.

Manganese is a common constituent of tungsten, iron, beryllium, titanium, and zinc ores, and its presence is readily detected in most acid decompositions and fusions.

CHAPTER XVIII

MANGANESE

I. JULIAN METHOD¹

A. Application

This is the most rapid method available for the determination of manganese in ores, as no filtrations and very few manipulations are necessary. The procedure is especially adapted to the rapid routine determinations of manganese ores containing appreciable amounts of manganese. It is not recommended for material containing only small amounts of manganese.

B. Interfering Elements

Chromium interferes, owing to its reduction by hydrogen peroxide in cold acid solution and only slow re-oxidation by permanganate. Elements such as vanadium, molybdenum, and nickel may cause trouble, when present in excessive amounts, on account of their color.

C. Procedure

a. Decompose 0.5 gram of the material, with 10 ml. of hydrochloric acid, in a 400-ml. beaker. Evaporate to a small volume, add 10 ml. of nitric acid, and again take down to a small volume. Add 15 ml. more nitric acid and 2 or 3 grams of potassium chlorate crystals, and boil carefully for about ten minutes, or until all free chlorine is removed.

b. Remove from the plate, and cool rapidly under the tap or in a cooling tray. Dilute to 200 ml. with cold water, and add a measured amount of hydrogen peroxide solution (850 ml. of water, 50 ml. of concentrated sulfuric acid, and 100 ml. of 3 per cent hydrogen peroxide) from a buret, while stirring, until all the MnO_2 is reduced and the solution is clear, and then about 10 ml. in excess.

¹ F. A. Julian, *J. Am. Chem. Soc.*, 15, 113, 1893.

Titrate the excess peroxide solution with standard potassium permanganate solution. Standardize the peroxide solution with the permanganate solution, and calculate on a basis of reduction of the manganese from a valence of four to two. The iron value of the permanganate multiplied by 0.4918 will give the manganese value. It is better, however, to standardize the solution with known material under the same conditions.

II. OXALIC ACID METHOD

A. Application

The method is applicable to ores and metallurgical products containing moderate to large amounts of manganese. In dealing with material which fails to be sufficiently decomposed by simple acid treatment, the mode of attack calls for the exercise of the operator's judgment. It is usual to employ one of the methods described under Iron I, C, b, c, d, e, or f, and eventually to bring the solution of the substance into a proper condition for continuing by the regular method.

B. Interfering Elements

Lead is the chief interference in this method. It is oxidized by the bromine to PbO_2 and precipitates with the manganese. Lead salts are not oxidized by nitric acid and potassium chlorate as used in the Julian method for the precipitation of MnO_2 .

C. Procedure

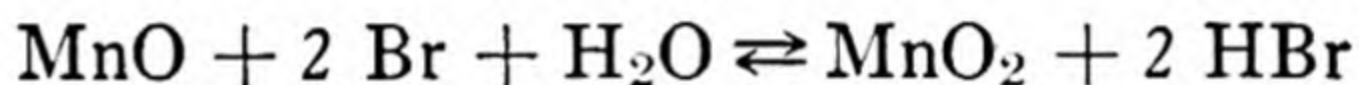
a. Treat 0.5 gram of the substance in an 8-oz. flask with whatever acids are necessary to decompose it. For an oxidized ore, about 10 ml. of strong hydrochloric acid is usually sufficient. With mixed ores it is best, ordinarily, to start with hydrochloric acid, to dissolve the oxides, and then add 5-10 ml. of strong nitric acid to decompose the sulfides. With pure, or nearly pure, sulfides, begin at once with 10 ml. of nitric acid.

b. Heat very gently at first until the decomposition is complete. Finally add about 5 ml. of strong sulfuric acid and heat strongly, best over a free flame, almost to dryness. Cool, and add about 100 ml. of water. Boil the mixture a moment and allow to stand, hot, with occasional shaking, until anhydrous ferric sulfate, etc., has dissolved (a minute or two). Add 1 or 2 grams of finely powdered

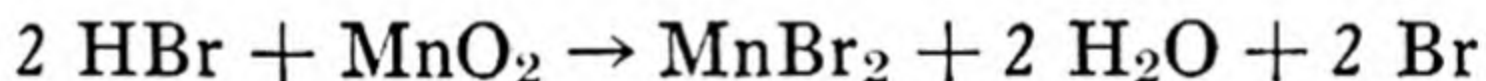
(not lumpy) zinc oxide, and heat to boiling. Remove from the heat and continue to add zinc oxide in small portions, while shaking, until all iron is precipitated and a moderate amount of white zinc oxide remains in the bottom of the flask. Be sure that all the iron is down. Heat to boiling (likely to foam), and then filter through an 11-cm. filter having a small wad of wetted absorbent cotton in the apex. Wash ten times with hot water, receiving the filtrate in a 600-ml. beaker. If any lead is likely to be present, add 2 ml. of a saturated potassium dichromate solution before the final boiling.

c. Add to the filtrate 3-4 grams of sodium acetate, or about 5 ml. of a saturated solution, and 30 ml. of saturated bromine water. Heat to boiling, and boil several minutes. If bromine vapors do not appear above the liquid in the covered beaker, add more bromine water until they do. This shows the necessary excess.

The following reaction gives the outline of how the bromine oxidizes and precipitates the manganese:



If the HBr were allowed to accumulate, the reaction might reverse as follows:



This is prevented by the sodium acetate. It neutralizes the hydrobromic acid and sets free acetic acid in its place. The acetic acid is without action on the precipitated MnO_2 .

d. Filter through an 11-cm. filter, and wash ten times with hot water. Any MnO_2 adhering in the beaker is simply washed clean and left there. It will be recovered later. The filtrate should be clear. If desired, it may be further tested by boiling with more bromine water.

e. Place the washed precipitate, together with the filter, back in the beaker, and run in from a buret what is judged to be an excess of the standard oxalic acid solution. On the basis of 0.5 gram of ore taken for assay, each milliliter of this solution is equivalent to about 1 per cent of manganese. Now add about 50 ml. of dilute 1 : 10 sulfuric acid and heat the mixture nearly to boiling with gentle agitation. Avoid shredding the filter. If the precipitate fails to dissolve completely, after boiling gently for some time, add more

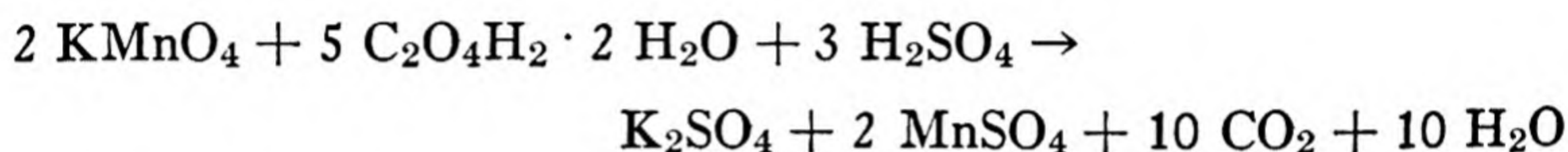
of the oxalic solution, but avoid a large and unnecessary excess. When the precipitate has entirely dissolved, dilute the solution to 150-200 ml. with hot water and titrate to a faint permanent pink tinge with a standard solution of potassium permanganate. The excess of oxalic acid not consumed by the MnO_2 is thus found. Subtracting this from the total amount of oxalic acid used, the remainder is the amount used in reducing the MnO_2 to MnO . The iron value of the permanganate times 0.4918 gives the manganese value.

The reactions that take place may be expressed as follows:

Between the MnO_2 and the oxalic acid:



Between the oxalic acid and permanganate:



The preparation of the standard solutions will be found in Chapter XXXIII.

III. VOLHARD'S METHOD²

A. Application

This is the method most generally used in western laboratories; it gives results accurate enough for technical purposes with a minimum expenditure of time. Like the preceding methods, it is not suited for ores in which small amounts of manganese are in question.

B. Interfering Elements

None of the commoner elements interfere in this method.

C. Procedure

a. Treat 1 gram of the ore in a 250-ml. beaker with whatever acids are necessary to decompose it, beginning with 10 ml. of strong hydrochloric acid, and heating very gently, if oxides are present, and afterwards adding nitric acid, if necessary, to decompose sulfides and peroxidize iron. When the decomposition is complete add about 7 ml. of strong sulfuric acid and heat over a free flame until

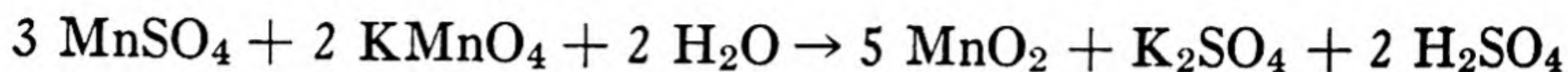
² J. Volhard, *Am. Chem.*, 198, 318, 1879.

fumes of sulfuric acid are evolved copiously. Cool, add 25 ml. of water, boil a short time, and allow to stand, hot, with frequent shaking, until all anhydrous ferric sulfate has dissolved. It is a good idea to add an oxidizing agent during this digestion, such as a crystal of potassium chlorate or a little bromine water, to make sure that the elements are in their higher valences.

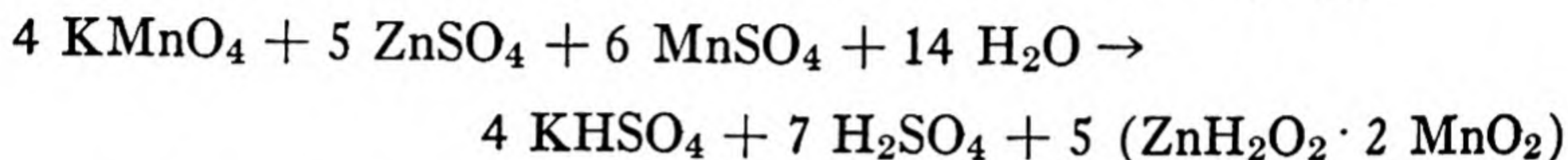
b. Transfer the mixture to a 500-ml. graduated flask, and add an emulsion of zinc oxide in slight excess, to precipitate the iron. Agitate the flask to facilitate the precipitation, and see that a slight excess of zinc oxide remains when the reaction is complete. Now dilute the contents of the flask up to the mark with cold water, mix thoroughly, and allow to stand a short time and partly settle.

c. By means of a graduated pipet draw off 100 ml. of the clear supernatant liquid and transfer it to an 8-oz. flask. Although the precipitate in the 500-ml. flask may appear large, it actually occupies but a very small space, and any error caused by it may consequently be neglected. Likewise the error in measurement due to change of temperature during the manipulation is insignificant. Heat the solution in the small flask to boiling, add 2 or 3 drops of nitric acid (which causes the subsequent precipitate to settle more quickly), and titrate with a standard solution of potassium permanganate. The permanganate causes a precipitate which obscures the liquid, and it is therefore necessary to titrate cautiously and agitate the flask after each addition, and then allow the precipitate to settle sufficiently to observe whether or not the solution is colored pink. A little experience will enable one to judge, by the volume of the precipitate formed, about how rapidly to run in the permanganate. The final pink tinge, indicating the end of the reaction, is best observed by holding the flask against a white background and observing the upper edges of the liquid. When this point is attained, bring the contents of the flask nearly to a boil once more and again observe whether the pink tint still persists, adding more permanganate if necessary. In making this end test avoid actually boiling the liquid, as a continual destruction of the color may sometimes thus be effected and the true end point considerably passed. When the color thus remains permanent the operation is ended. Observe the number of milliliters of permanganate solution used, and calculate the percentage of manganese.

The precipitate formed is not necessarily manganese dioxide, although the calculation can be correctly made as though the following reaction took place:



In the presence of metallic salts, such as those of calcium or zinc, manganites of varying compositions are formed, e.g.,



The precipitated manganese, however, is always in the tetravalent form, and, therefore, the ratio of the first reaction between the manganese and the permanganate is not changed.

The iron value multiplied by 0.2951 will give the manganese value.

IV. BISMUTHATE METHOD³

A. Application

This method is based on the fact that a manganous salt in the presence of an excess of nitric acid is oxidized to permanganic acid by bismuth tetroxide. The permanganic acid formed is very stable in nitric acid of 1.135 sp. gr. when the solution is cold, but in hot solution the excess of the bismuth tetroxide is rapidly decomposed; then the nitric acid reacts with the permanganic acid, and as soon as a small amount of manganous salt is formed the remainder of the permanganic acid is decomposed, manganous nitrate dissolves, and manganese dioxide precipitates.

In the cold, however, the excess of the bismuth salt may be filtered off, and to the clear filtrate an excess of ferrous sulfate may be added and the amount necessary to deoxidize the permanganic acid determined by titrating with permanganate. The end reactions are very sharp, and the method is extremely accurate, especially for low-grade material.

B. Interfering Elements

Elements, such as chromium and vanadium, that are reduced by ferrous sulfate may cause trouble in the titration. Hydrochloric

³ Andrew A. Blair, *J. Am. Chem. Soc.*, 27, 793, 1905. Method originally proposed by Schneider and modified first by Reddrop and Ramage and then by Brearley and Ibbotson.

acid or free chlorine, which have a reducing action on manganese, must be absent. Lundell⁴ states that cobalt is oxidized to an indefinite stage and must be separated when this method is used.

C. Procedure

a. *Pig Iron.* Dissolve 1 gram in 25 ml. of nitric acid, sp. gr. 1.135 (1 part of strong nitric acid to 3 parts of water), in a small beaker, and, as soon as the action has ceased, filter on a 7-cm. filter into a 250-ml. beaker, wash with 30 ml. of the same acid, and proceed as in f.

In the analysis of white irons it may be necessary to treat the solution several times with bismuthate to destroy the combined carbon. The solution, when cold, should be nearly colorless; if it is not, another treatment with bismuthate is necessary.

b. *Iron Ores Containing Less Than 2 Per Cent of Manganese.* Treat 1 gram in a platinum dish or crucible with 4 ml. of strong sulfuric acid, 10 ml. of water, and 10 to 20 ml. of hydrofluoric acid. Evaporate until the sulfuric acid fumes freely. Cool and dissolve in 25 ml. of 1.135 nitric acid. If no appreciable residue remains, transfer to a 250-ml. beaker, using 25 ml. of 1.135 nitric acid to rinse the dish or crucible, and proceed as usual. If there is an appreciable residue, filter on a small filter into a beaker, wash with water, burn the filter and residue in a crucible, and fuse with a small amount of potassium acid sulfate. Dissolve in water with the addition of a little nitric acid, add to the main filtrate, evaporate nearly to dryness, and take up in 1.135 nitric acid.

c. *Manganese Ores and Iron Ores High in Manganese.* Treat 1 gram like the iron ores, using a little sulfurous acid if necessary. Transfer the solution to a 500-ml. flask, dilute to the mark, mix thoroughly, and measure into a flask, from a carefully calibrated pipet, such a volume of the solution as will give from 1 to 2 per cent of manganese and enough strong nitric acid (sp. gr. 1.4) to yield a mixture of 1.135 acid in a volume of 50 to 60 ml. For example, in a 50 per cent ore use 10 ml. of the solution and add 30 ml. of water and 10 ml. nitric acid (sp. gr. 1.4). The manganese must then be calculated on $\frac{1}{50}$ gram or 20 mg. of ore. When working on such amounts it is always desirable to make duplicate analyses

⁴ G. E. F. Lundell, *J. Am. Chem. Soc.*, 45, 2600, 1923.

and take the mean, as a difference of 0.1 ml. makes a large error in the result. When the ore contains a much smaller amount of manganese, say 5 to 10 per cent, it is better to make up the solution to 100 ml. instead of 500.

d. *Ferromanganese*. Treat 1 gram with 50 ml. of nitric acid. Dilute to 500 to 1000 ml., and proceed as in manganese ores.

e. *Ferrosilicon*. Treat 1 gram with sulfuric and hydrofluoric acids, and proceed as with iron ores.

f. To the solution from a, b, c, d, or e, after cooling, add about 0.5 gram of bismuthate. The bismuthate may be measured in a small spoon; experience will soon enable the operator to judge the amount with sufficient accuracy. Heat for a few minutes, or until the pink color has disappeared, with or without the precipitation of manganese dioxide. Add sulfurous acid, solution of ferrous sulfate, or sodium thiosulfate in sufficient amount to clear the solution, and heat until all nitrous oxide has been driven off. Cool to about 15° C., add an excess of bismuthate, and agitate for a few minutes. Add 50 ml. of water containing 30 ml. of nitric acid to the liter, filter through an asbestos felt on a platinum cone into a 300-ml. Erlenmeyer flask, and wash with 50 to 100 ml. of the same acid. Run into the flask, from a buret, a measured volume of ferrous sulfate solution, and titrate to a faint pink color with permanganate. The number of milliliters of the permanganate solution obtained, subtracted from the number corresponding to the volume of ferrous sulfate used, will give the volume of permanganate equivalent to the manganese in the sample, which, multiplied by the value of the permanganate in manganese, gives the amount of manganese in the steel. One milliliter of 0.10 *N* KMnO_4 is equivalent to 0.001099 gram Mn, or the iron value multiplied by 0.1967 equals the manganese value.

V. COLORIMETRIC METHOD

A. Application

For the determination of minute amounts of manganese in materials like limestone or clay, a colorimetric method is desirable. Manganese is oxidized readily to permanganic acid by potassium periodate,⁵ and the colored solution is quite stable.

⁵ H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, **39**, 2366, 1917.

B. Interfering Elements

The solution must be free of reducing agents, such as carbonaceous material, or hydrochloric acid.

C. Procedure

Obtain a clear solution containing 20 per cent nitric, 10 per cent sulfuric, and 5 per cent phosphoric acids. If acid decomposition of the material is used, finish by fuming with sulfuric acid to remove chlorides. Ammonia precipitates may be dissolved in sulfuric acid or fused with potassium bisulfate.

Add 0.25 gram of potassium periodate, heat to boiling, and digest for a few minutes. Cool and transfer to a comparison tube, and dilute to the mark. Compare the magenta color with standard comparison solutions prepared from potassium permanganate.

MERCURY MINERALS

Mineral Name	Chemical Formula	% Hg	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Cinnabar.....	HgS	86.2	Scarlet-red to brownish red	8.1	Si, Ca, Fe, C, Cu, As, Sb, Pb, Ag, Au	Hot H ₂ SO ₄	
Native Hg.....	Hg	13.6	Ag	HNO ₃	

Mercury is seldom encountered in ore analysis in minerals other than cinnabar. The selenides, tiemannite and onofrite, and the telluride, coloradoite, may occasionally be encountered.

Cinnabar is readily soluble in aqua regia with separation of sulfur, but, owing to the volatility of the chloride, hydrochloric acid or combinations evolving chlorine are best to be avoided with acid decompositions. Mercury may also be volatilized in fusions with sodium carbonate.

CHAPTER XIX

MERCURY

I. VOLUMETRIC THIOCYANATE METHOD ¹

A. Application

The following procedure is especially adapted to mercury ores and products which contain an appreciable amount of mercury.

B. Interfering Elements

Elements that form precipitates with soluble thiocyanates include (in addition to bivalent mercury) silver, quadrivalent palladium, monovalent copper, bivalent lead, monovalent thallium, bivalent tin, and monovalent mercury. Double salts are also formed by mercury with elements such as zinc, cadmium, copper, and cobalt.

C. Procedure

a. Weigh 1 gram, more or less, of the ore, according to richness, into an 8-oz. flask. Add 10 ml. of 1 : 1 sulfuric acid and about 0.5 gram of potassium permanganate crystals. Agitate the flask and heat to boiling, finally boiling to fumes. Allow to cool, then dilute with about 50 ml. of cold water, heat to boiling, and, while boiling, add oxalic crystals, a little at a time, until all the separated MnO_2 is reduced and dissolved. Cool under the tap and filter, washing with dilute (1 : 10) sulfuric acid.

b. Pass hydrogen sulfide into the cold filtrate to saturation. Filter, washing with cold water. Rinse the precipitate from the filter (while still in the funnel), as completely as possible, into a porcelain dish or casserole, and boil it for some time with dilute nitric acid (2 : 1). Finally, dilute the mixture with a little hot water and filter through the same filter as before, washing with hot dilute nitric acid (1 : 3). The filter will probably be more or less stained with sulfides that could not be rinsed off. The hot filtration

¹ A. H. Low, *Chemist-Analyst*, 29, 13, 1919.

and washing will tend to cleanse these traces of sulfides, so that any impurities finally left with the HgS will be negligible.

c. Wash the well-washed sulfide from the filter into an 8-oz. flask, with hot water, using as little as possible. The stain remaining on the filter may generally be neglected. Save the filter, however. To the mixture in the flask add 5-6 ml. of strong sulfuric acid and 0.5 gram, or usually less, of potassium permanganate crystals. Boil with frequent agitation over a free flame to fumes. Now remove from the heat, and, without cooling, add oxalic crystals, in very small portions so as to avoid much excess, until all the separated MnO_2 is reduced and dissolved. Again heat to fumes to destroy the excess of oxalic acid. Cool and then dilute with about 100 ml. of cold water. The solution should be perfectly clear.

d. Cool to room temperature, add the usual ferric indicator (about 5 ml. of a strong solution of ferric ammonium sulfate, acidified with nitric acid to decolorize), and titrate with standardized, approximately 0.1 N thiocyanate solution to the usual faint brownish tint. One milliliter of 0.1 N thiocyanate = 0.01003 gram Hg.

Standardize the thiocyanate as described in Chapter XXXIII.

If the stain on the filter paper is worth recovering, spread the wet paper on a watch glass, sprinkle on a little powdered permanganate, add a little 1 : 1 sulfuric acid, and warm a moment. Now add a very little dry oxalic acid, warm again to dissolve any MnO_2 , and then rinse the solution into the flask containing the balance of the sulfide, continuing as above in c.

II. HOLLOWAY-ESCHKA METHOD²

A. Application

This method is particularly applicable to low-grade ores and is valuable on a semi-micro scale as a qualitative test for mercury.

B. Interfering Elements

Elemental sulfur and ores liberating much sulfur upon heating will blacken silver foil. Gold foil decreases the interference but the mercury will still be contaminated. Organic matter and combined H_2O in quantity interfere with the amalgamation of the mercury to the silver or gold foil.

² A. Eschka, *Z. anal. Chem.*, 2, 344, 1863; G. T. Holloway, *Analyst*, 31, 66, 1906.

C. Procedure

Mix 0.2 to 5 grams of the ore with 1 to 10 grams of iron filings in a porcelain, iron, or nickel crucible of suitable size. Clamp the crucible tightly in an apparatus such as shown in Fig. 13 with a weighed piece of clean sheet silver or gold. Carefully heat the lower part of the crucible with a Bunsen burner, keeping the foil cold with a steady stream of water passing through the condenser. The ring of asbestos board fitted around the crucible at the proper height will assist materially in preventing the top from getting overheated. It will require from ten to thirty minutes to distil off the

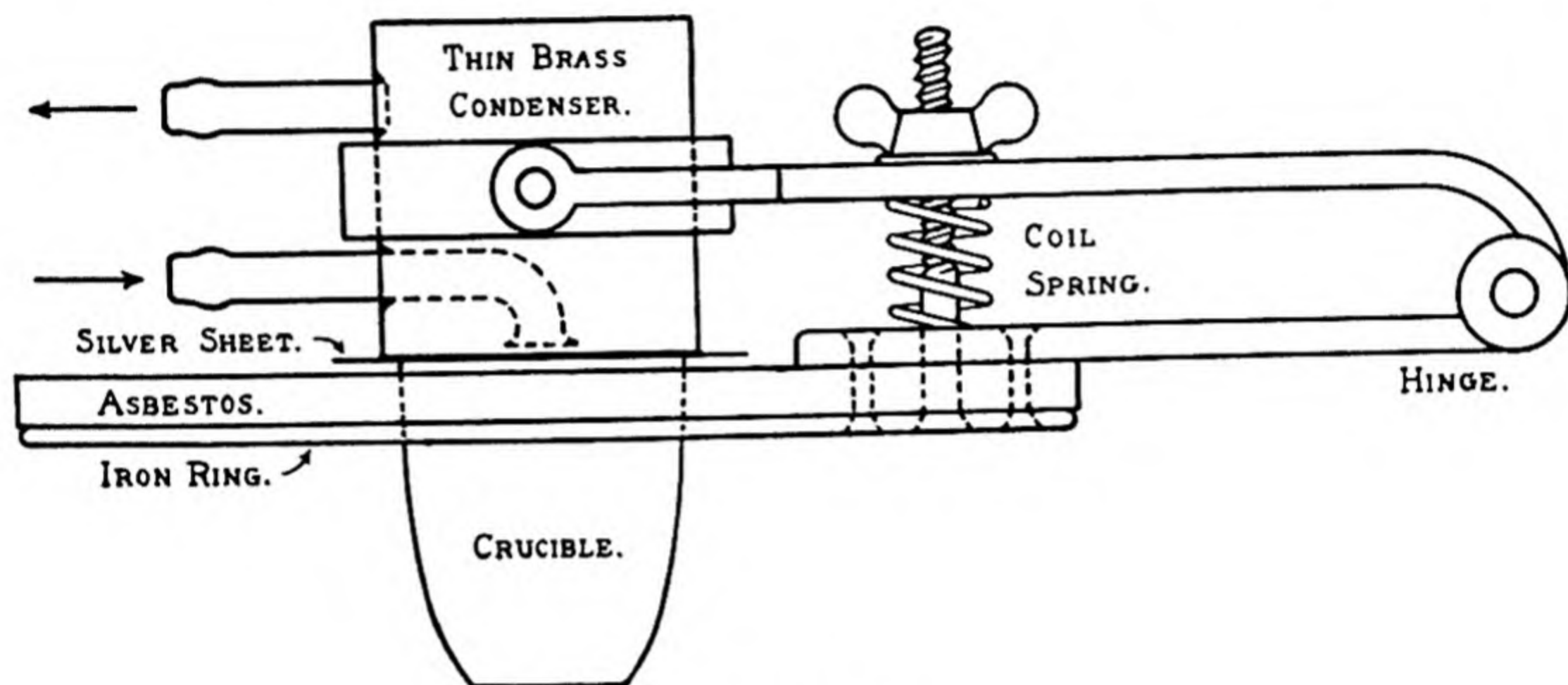


FIG. 13.

mercury. When the operation is considered ended, allow the crucible to cool, remove the silver or gold cover, dip in alcohol, dry carefully without heating, and weigh. The increase in weight of the silver or gold cover represents the weight of mercury.

It is best to have a thin layer of iron filings over the charge.

Sulfide ores containing arsenic are best mixed with double their weight of a mixture of 4 parts zinc oxide and 1 part sodium carbonate, together with iron filings 5 times the weight of the ore.

MOLYBDENUM MINERALS

Mineral Name	Chemical Formula	% Mo	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Molybdenite.....	MoS ₂	60.0	Bluish gray, shining, greasy feel	4.8	W, Fe, Cu, F, Si, Ca, Bi, Sn	HNO ₃ + KClO ₃ Aqua regia	Na ₂ CO ₃ + Na ₂ O ₂
Wulfenite.....	PbMoO ₄	26.2	White to yellow	7.0	Ca, Zn, Fe, W, Si	HCl + H ₂ SO ₄	Na ₂ CO ₃ + Na ₂ O ₂
Molybdic ocher...	Fe ₂ O ₃ ·3MoO ₃ ·nH ₂ O	Variable	Bright yellow	4.5	Same as above	HCl	Same as above
Powellite.....	Ca(MoW)O ₄	Variable	Yellow to greenish	4.3	Same as above	Aqua regia	Same as above

Molybdenum is most often encountered as the sulfide, molybdenite. Molybdenite is dissolved slowly by nitric acid with almost complete separation of the molybdenum as MoO₃ upon evaporation. Acid decompositions using nitric acid should therefore always be followed by digestion with hydrochloric or sulfuric acid to insure complete solution of the molybdenum. Lead sulfate precipitated by sulfuric acid decompositions, and tungstic acid precipitated in acid digestions, will always carry down small amounts of the molybdenum, and require subsequent recoveries. The common analytical reactions of molybdenum are seriously affected when the molybdenum is in reduced forms. Quantitative separations of molybdenum proceed according to theory only when the molybdenum is kept in the sexivalent state.

CHAPTER XX

MOLYBDENUM

I. LEAD MOLYBDATE METHOD¹

A. Application

This is an accurate and rapid method for molybdenite ores of all grades, but subject to numerous interferences.

B. Interfering Elements

The chief interfering elements are those which form: (1) insoluble molybdates, or (2) insoluble lead salts in ammonium acetate-acetic acid solution. Those of the first class include lead, thallium, silver, barium, strontium, and calcium. All these, except calcium, and presumably strontium, interfere seriously, even in small amounts. Calcium gives a low result only when present in excessive amounts. Those of the second class, which combine with lead to form insoluble salts, are arsenates, phosphates, chromates, tungstates, vanadates, and fluorides. Moderate amounts of fluorine do not interfere if enough calcium is present to carry it out in the ammonium hydroxide precipitate as calcium fluoride. Sulfates (which are always present owing to the oxidation of sulfides during decomposition) produce low results when present in excess, probably caused by an increase in the solubility of the lead molybdate formed. The effect of sulfates is rendered negligible by increasing the ammonium acetate-acetic acid ion concentration. Small amounts of arsenic, antimony, phosphorus, tungsten, and vanadium may be handled if sufficient iron is present to carry them out with the ammonium hydroxide precipitate. Mercury, boron, copper, zinc, cadmium, manganese, iron, aluminum, magnesium, cobalt, and nickel

¹ Method of the Climax Molybdenum Company, Climax, Colorado.

do not interfere under ordinary conditions. When the ammonium hydroxide precipitate is very bulky it is difficult to remove all the molybdenum even with double precipitations.

C. Procedure

a. Weigh 0.25 to 5 grams of the ore, and transfer to a 400-ml. beaker. Moisten the material with water, and add 20 ml. of nitric acid saturated with potassium chlorate. With concentrates or material high in sulfides, the amount of water must be increased and the saturated acid added cautiously to avoid a too violent reaction. Cover the beaker, bring the contents to a boil, and digest at a temperature just below boiling for 20 to 40 minutes according to the amount of sulfides present. Lift the cover glass, and allow the contents to evaporate to about 10 ml. Remove from the plate, cover, and add 10 ml. of hydrochloric acid. Heat to boiling and boil down to a volume of about 5 ml. Again remove from the hot plate, add 10 ml. of hydrochloric acid and a small crystal of potassium chlorate; wash the cover glass and sides of the beaker with a fine stream of water, and dilute to 75 ml.

b. Heat till all the soluble salts are in solution. Add ammonium hydroxide from a dispensing buret, while whirling the solution in the beaker, until alkaline, and then 25 ml. in excess. Boil vigorously for 5 to 10 minutes, and filter on a 11-cm. paper, catching the filtrate in a 600-ml. beaker. Wash the precipitate with hot water. Transfer the bulk of the precipitate back to the beaker and place the beaker under the funnel. Dissolve the remainder of the precipitate adhering to the filter paper with hot (1 : 1) hydrochloric acid, and wash the paper thoroughly with hydrochloric acid and hot water, finally finishing with a 2 per cent ammonium hydroxide wash.

Reprecipitate the acid solution with ammonium hydroxide as before, using 25 ml. excess. Boil, and filter through the same paper as before, receiving the filtrate with that from the first precipitation. Wash well with boiling hot water. The volume of the filtrate will now be about 300 ml.

c. Neutralize the filtrate with hydrochloric acid, using methyl orange as indicator, and add 3 or 4 drops in excess. Add 20 ml. of

ammonium acetate-acetic acid solution (250 ml. of saturated ammonium acetate solution and 150 ml. of glacial acetic acid per liter). In the presence of large amounts of sulfates, increase the amount added to 40-60 ml. Heat the solution to boiling, and titrate with lead acetate solution (18 grams of lead acetate and 15 ml. of glacial acetic acid per liter), drop by drop, with vigorous stirring, until a drop of the solution tested with a drop of tannic acid solution as an outside indicator no longer shows a yellow color. Then, run in 1.5 ml. of the lead acetate solution in excess. Stir in about 0.25 gram of paper pulp, and boil for a few minutes. Allow to digest on a cooler portion of the plate until the precipitated lead molybdate has settled and the solution is clear.

d. Filter off the precipitate on a 11-cm. ashless paper and wash with water containing 50 ml. of the ammonium acetate-acetic acid solution per liter. Scrub the beaker well with a rubber policeman to remove the adhering precipitate. Fold the paper and precipitate, and place in a No. 00 black-lined porcelain crucible. Dry, ignite at a dull red heat, and weigh as PbMoO_4 . The residue should be white or only faintly yellowish.

Multiply the weight of lead molybdate by 0.2613 to obtain the weight of molybdenum.

D. Modifications

a. In the presence of interfering elements, the molybdenum may be separated as the sulfide. The separation is more satisfactory when the sulfide is precipitated from alkaline sulfide solution by the slow addition of acid (see **Procedure II, C, c**), and provides for the exclusion of elements such as lead, thallium, silver, phosphorus, chromium, tungsten, and vanadium. The molybdenum sulfide is ignited to MoO_3 at a low heat and treated as described for the original material in **C, a**. Arsenic and fluorine are most easily removed by volatilization during the decomposition, which may be modified accordingly.

b. For material containing less than 10 per cent of molybdenum, by far the best separation from interfering elements (except tungsten) is by precipitation with α -benzoinoxime. For details, see **Procedure III**.

II. VOLUMETRIC METHOD

A. Application

This method is satisfactory for ores and metallurgical products containing moderate amounts of molybdenum. Low-grade materials are best treated by Procedures I or III.

B. Interfering Elements

Excessive amounts of elements such as tungsten, vanadium, chromium, and iron that are reduced by zinc in sulfuric acid solution and oxidized by permanganate may contaminate the final solution (owing to incomplete separations) and cause high results.

C. Procedure

a. Weigh 0.5 gram of the finely ground material. Place in a thin spun-iron crucible of about 25- to 30-ml. capacity, and mix with 1 gram of sodium carbonate. Add about 6 grams of sodium peroxide, and again mix well.

Holding the crucible with tongs, fuse over a Bunsen burner, heating slowly at first and gradually bringing to dull redness. Rotate the crucible as the mixture melts, so as to obtain a perfect fusion without overheating and destroying the crucible. A low red heat is all that is necessary. With a bright red the iron is likely to be strongly attacked and the crucible perforated. The initial melting of the mass is slow, but a low red heat, persisted in, will eventually bring it to perfect fluidity.

The same crucible should serve for many fusions (cf. Chromium I, C, a). The sodium carbonate is used solely to moderate the action of the peroxide. With oxidized material it is unnecessary, but without it sulfides may scintillate and spatter, or even deflagrate. Add more or less than 1 gram, according to judgment or trial.

b. After the fusion, allow to cool to a crust on top and then set the crucible in a 400-ml. beaker containing about $\frac{3}{4}$ inch of cold water. Cover the beaker, and then upset the crucible with a glass rod. Disintegration usually occurs quickly without further heating. Remove and rinse the cover, and then lift out the crucible with the glass rod and wash it.

Add 10 grams of ammonium carbonate, which should be suffi-

cient to neutralize all the fixed alkali and leave an excess. Warm until all the ammonium carbonate is dissolved, then filter (best with a Witt's plate and suction), and wash at least ten times with hot water.

Add about 2 grams of tartaric acid or a tartrate (Rochelle salts) to the filtrate, which should still remain strongly alkaline. This is to prevent precipitation of tungsten or vanadium when the solution is subsequently acidified.²

c. Saturate the hot alkaline liquid with hydrogen sulfide gas. A purple solution, at this point, indicates the presence of considerable vanadium. Molybdenum gives a yellow to orange solution, becoming brown on prolonged treatment, owing to reduction. Reduction of the molybdenum must be avoided as much as possible, as the reduced compound will not be precipitated on acidification.

Acidify the solution, slowly, with sulfuric acid (1 : 1) while bubbling the H_2S through the hot liquid. The molybdenum will come down as a brown flocculent precipitate. Filter off the molybdenum sulfide and wash five or six times with hot water. The filtrate may still contain a little molybdenum. Make it alkaline again with ammonium hydroxide and boil for about five minutes. Add a few drops of hydrogen peroxide, and again saturate with hydrogen sulfide, then acidify and filter as before, using a second filter.

Place both filters and their contents back in the 400-ml. beaker, cover, and add 5 ml. of sulfuric acid and 10 ml. of nitric acid. Take to fumes on the hot plate, and completely oxidize the paper by repeated additions of nitric acid, finally heating strongly to expel the nitric acid.

d. After cooling, take up the residue in about 150 ml. of warm water, and add 3 ml. of a 4 per cent solution of copper sulfate. Now cautiously add, a little at a time at first, 5 grams of 30-mesh zinc, and cover the flask with a watch glass. If the action is too violent, cool the flask to prevent foaming over. Later, the flask may be warmed if necessary. Allow the action to proceed, warm, for about fifteen minutes. This should precipitate all the copper and, incidentally, any arsenic present. Zinc alone, without added copper, will not remove all the arsenic. Now add a little sulfuric acid, to

² Steřba-Böhm and Vostřebel, *Z. anorg. Chem.*, 110, 81, 1920, recommended the use of formic acid for this separation.

make certain that the liquid is still acid, and filter. Wash the residue with cold water.

e. To the filtrate add 20 ml. of 1 : 1 sulfuric acid. Pour the hot solution through the reductor in accordance with the following directions:

The reductor tube should have at least an 8-inch zinc column, $\frac{5}{8}$ inch in diameter, using 20- to 30-mesh amalgamated granulated zinc. The end of the reductor tube should be prolonged to reach nearly to the bottom of the receiving flask. The flask (32-oz.) should contain 30-35 ml. of ferric phosphate solution,³ and the end of the reductor tube should dip below this, so that the reduced molybdenum solution is not exposed to the air but is oxidized at the expense of the ferric phosphate.⁴ The molybdenum solution should contain about 5 ml. of free sulfuric acid per 100 ml. and should be passed rather slowly (about five minutes) through the reductor, at a temperature of 50°-75° C. After passing the molybdenum solution, the reductor should be washed by passing 100 ml. of hot water containing 5 ml. of strong sulfuric acid, followed by hot water alone. The titration with the permanganate (of the strength generally used for iron) should be made in the warm solution immediately after reduction. With sufficient molybdenum present, the liquid in the receiving flask is red. As permanganate is added, the red slowly fades and the solution becomes colorless; then the final pink which follows is easily recognized. A blank should be made, beginning with 150 ml. of water and 5 ml. of sulfuric acid in an 8-oz. flask, adding the copper sulfate and zinc in d and continuing as there described. The usual correction obtained in this way is about 0.20 ml. of permanganate solution.

Under the above conditions the reduction is from MoO_3 to Mo_2O_3 , and is exact. Refer to **Chapter XXXIII** for the preparation and standardization of the permanganate solution.

The Fe factor of the permanganate multiplied by 0.5732 gives the Mo factor. Mo multiplied by 1.6683 = MoS_2 .

³ Dissolve 100 grams of ferric ammonium sulfate in 500 ml. of water, adding 25 ml. of strong sulfuric acid, followed by 150 ml. of syrupy (85 per cent) phosphoric acid, and diluting to 1000 ml.

⁴ When ferric phosphate is used, it is actually iron and not molybdenum that is titrated. The ferric salt does the oxidizing previous to the titration, and a corresponding amount of ferrous salt is formed; this is then titrated with permanganate.

III. α -BENZOINOXIME METHOD ⁵

A. Application

This method is excellent for low-grade material (preferably 5 per cent molybdenum or less). It is both rapid and accurate and is much less subject to interferences than the preceding methods.

B. Interfering Elements

Tungsten is the most common interfering element, owing to its frequent association with molybdenum in ores. Small amounts of tungsten are precipitated quantitatively with the molybdenum by α -benzoinoxime; large amounts will cause low results by carrying down of molybdenum with the tungstic acid which separates with insoluble material. Vanadium and chromium interfere only when present in their higher valences, and lead separating as lead sulfate in sulfuric acid decompositions will be contaminated by molybdenum and cause low results. Silica is almost always present in the final precipitate of MoO_3 , but is easily corrected for.

C. Procedure

a. To the finely ground sample (containing not more than 50 mg. of molybdenum), in a 400-ml. beaker, add 5 to 10 ml. of water and 20 ml. of nitric acid saturated with potassium chlorate. Heat to boiling, and allow to digest at a temperature just under boiling for fifteen to twenty minutes. Cautiously add 10 ml. of sulfuric acid, and take rapidly to fumes. Cool, wash the cover glass and sides of the beaker, dilute to 75 ml., stir in 0.25 gram of paper pulp, and heat till the soluble salts are well in solution. Filter on a close paper, and wash well with 5 per cent sulfuric acid. Receive the filtrate in a 400-ml. beaker. Examine the insoluble residue for tungstic acid, lead sulfate, and any undecomposed material. Test a drop of the solution for vanadium and chromium (**Chapter I**).

b. Cool the filtrate rapidly by adding two crushed ice cubes. To the cold solution add 10 ml. of a 2 per cent solution of α -benzoinoxime in 95 per cent ethyl alcohol. Stir with a glass rod, and add saturated bromine water until the solution is decidedly yellow.

⁵ H. B. Knowles, *Nat. Bur. Standards J. Research*, 9, 1, 1932, by permission of G. E. F. Lundell.

Add 5 ml. to 10 ml. more of the oxime solution, according to the amount of precipitate, stir, and allow the precipitate to coagulate well. Stir in a little paper pulp, and filter on a close ashless paper. The solution should be kept oxidized and cold during the filtration, more ice or bromine water being added as necessary. Wash the precipitate thoroughly with ice water containing 5 ml. of sulfuric acid and 10 ml. of the oxime solution per liter. Draw off the excess wash solution, retained by the precipitate, by means of a suction flask and aspirator.

c. Fold the filter paper so that the main portion of the paper is above the precipitate, press flat between the fingers, and set in a No. 00 black-lined porcelain crucible so as to hang about halfway up the wall of the crucible. This is to avoid overheating the precipitate on the bottom of the crucible and allows a circulation of air under the precipitate. Dry and char the contents of the crucible on the hot plate, or place in a cold muffle and bring slowly to a temperature between 500° and 525° C. As MoO_3 starts to sublime at 550° C., care must be exercised not to overheat during ignition or the entire analysis may be lost. The residue of MoO_3 should be pure white or only faintly green or blue in color. Occasionally the residue has a gray or bluish gray appearance due to partial reduction of the molybdenum to Mo_2O_3 . This will cause trouble when dissolving the residue with ammonia. Continued heating with free access to the air will usually oxidize all the molybdenum to MoO_3 . Cool, and weigh as impure MoO_3 .

d. Place the weighed residue in a 150-ml. beaker, and add 20 ml. of water and 10 ml. of ammonium hydroxide. Heat to boiling, and filter on a 7-cm. ashless paper. Wash thoroughly with boiling hot water. Dry, ignite, and weigh the insoluble material. Deduct this weight from that of the impure MoO_3 to obtain the weight of MoO_3 . The weight of MoO_3 multiplied by 0.6665 will give the weight of molybdenum.

D. Modifications

a. In the presence of appreciable amounts of lead, the sulfuric acid treatment in the decomposition should be omitted. Obtain a hydrochloric acid solution containing from 10 to 15 ml. of free hydrochloric acid as described in Procedure I, C, a.

b. When vanadium or chromium is present the bromine water treatment should be omitted. Oxidize the cooled acid solution with potassium permanganate until faintly pink. Add 5 ml. of sulfurous acid to reduce the vanadium or chromium, and continue with the precipitation of the molybdenum with α -benzoinoxime, omitting the addition of bromine water.

c. Tungsten requires added treatment of the MoO_3 residue. Leach the insoluble residue obtained in C, a, with hot dilute ammonia, and catch the dissolved tungstic acid with the main filtrate. The final residue of impure MoO_3 with WO_3 is dissolved in ammonium hydroxide and filtered from the insoluble as described in C, d. Dilute the filtrate to 150 ml., add 2 grams of tartaric acid, and precipitate the molybdenum as the sulfide as described in Procedure II, C, c. Ignite the filtered MoS_2 at a temperature not exceeding 500°C. , and weigh the MoO_3 direct.

NICKEL MINERALS

Mineral Name	Chemical Formula	% Ni	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Nickeliferous-pyrrhotite	$\text{Fe}_n\text{S}_{n+1}$	0-6.0	Grayish black, metallic luster	4.6	Cu, Mg, Al, Si	HNO_3 , HCl	
Pentlandite.....	$2\text{FeS}\cdot\text{NiS}$	22.0	Light bronze-brown	5.0	Co, S, Sb, Ag, Cu, Ba, Si	HNO_3	
Garnierite.....	$\text{H}_2(\text{NiMg})\text{SiO}_4\cdot n\text{H}_2\text{O}$	Variable 2-35	Greenish white	2.3-2.8	Cr, Fe, Co, Al	HCl	Na_2CO_3
Millerite.....	NiS	64.7	Greenish black, metallic luster	5.6	Co, Ag, Fe, Ca, Mg, Al, F, Mn, Si	HNO_3	
Niccolite.....	NiAs	43.9	Light brownish black, metallic luster	7.6	Fe, Co, S, Sb, Ag, Cu, Ba, Si	Aqua regia	
Chloanthite-smaltite....	$(\text{NiCo})\text{As}_2$	Variable	Grayish black, metallic luster	5.7-6.8	Co, Ag, Cu, Zn, Pb, Fe, Bi	HNO_3	
Annabergite.....	$\text{Ni}_3(\text{AsO}_4)_2\cdot 8\text{H}_2\text{O}$	29.3	Greenish white	3.0	Fe, Co, S, Sb, Ag, Cu, Mg	HNO_3 , HCl	

Nickel is usually associated with basic rocks such as gabbro, norite, hornblende, augite, peridotite, and diorite. It is found in combination with tellurium in melonite; with antimony in breithauptite, corynite, ullmanite, etc.; and with cobalt in siegenite, skutterudite, linnaeite, etc.

No trouble is ordinarily encountered in the decomposition of nickel minerals, and its presence in solution is readily recognized by the colors of its salts, which may be confused for copper.

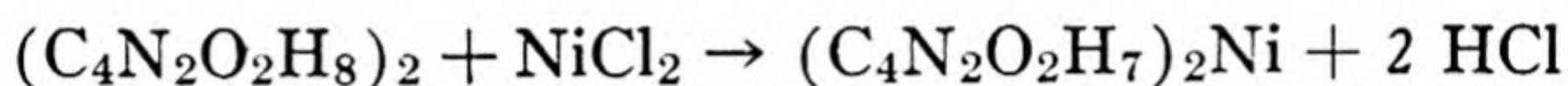
CHAPTER XXI

NICKEL

I. DIMETHYLGLYOXIME METHOD¹

A. Application

The reaction between nickel and dimethylglyoxime may be represented as follows:



The nickel dimethylglyoxime precipitate is extremely bulky and is not conveniently handled with material containing over 10 to 15 per cent of nickel. The method, however, is rapid and accurate for smaller amounts of nickel.

B. Interfering Elements

None of the common elements, when present in moderate amounts, offer any difficulties. Excessive amounts of elements that hydrolyze readily, and tungsten, silicon, cobalt, and copper, may cause trouble and had best be removed by preliminary separations.

C. Procedure

a. Decompose a weight of sample containing not more than 40 mg. of nickel by an appropriate acid digestion. Nitric acid saturated with potassium chlorate, or treatment with nitric and hydrochloric acids, will serve for most ores. With silicates it may be necessary to apply a sodium carbonate fusion to the insoluble residue. Evaporate the decomposed sample to dryness, take up the residue with 5 to 10 ml. of hydrochloric acid, and again evaporate to dryness. Add 5 ml. of hydrochloric acid and 100 ml. of water, and heat until all soluble salts are in solution.

¹ O. Brunck, *Z. angew. Chem.*, 20, 834, 1907.

b. Without cooling, pass in hydrogen sulfide for about ten minutes. Filter through a 9-cm. filter from the sulfides of arsenic, antimony, copper, etc., washing with hydrogen sulfide water. Receive the filtrate in a beaker.

Boil the filtrate until the hydrogen sulfide is expelled, then add a little bromine water to oxidize the iron and boil off the excess. When only small amounts of the elements of the hydrogen sulfide group are present, the precipitation with H_2S may be omitted, and the insoluble simply filtered out and washed well with hot water.

c. Now add 2 grams of tartaric acid (to keep iron in solution) and 2 grams of ammonium chloride (to keep manganese and zinc in solution). Make slightly alkaline with ammonia. If a cloud forms, add more ammonium chloride until clear. See that the liquid remains slightly alkaline.

d. Heat nearly to boiling. Add dimethylglyoxime in 1 per cent alcoholic solution, until the weight of the reagent is about seven times the assumed weight of the nickel present. Add ammonia, if necessary, until a faint but distinct odor is apparent. Stir well, and then set the beaker in a hot place for about fifteen minutes. Filter the hot mixture through a weighed Gooch crucible, and wash well with hot water.

e. Dry in an oven at $110^\circ\text{--}120^\circ\text{C}$. to constant weight. The scarlet-red nickel compound is nickel dimethylglyoxime. It has the formula $(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2\text{Ni}$ and contains 20.32 per cent of nickel.

f. Cobalt does not interfere unless it is present in considerable amount. If more than 0.1 gram is present, a large excess of dimethylglyoxime is necessary to keep it in solution, and more time should be allowed before filtering off the nickel dimethylglyoxime as its precipitation is retarded.

Theoretically, about 4 parts of dimethylglyoxime are required for 1 part of nickel, but an excess is always advisable. An excess does no harm unless the alcohol of the reagent solution exceeds more than one-half the volume of the aqueous nickel solution, when the alcohol has a slight solvent action on the precipitate.

II. ELECTROLYTIC METHOD

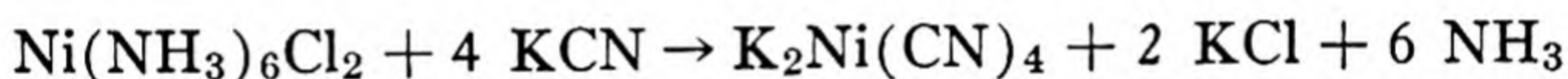
Proceed as given under Cobalt, II, C, a, b, c, and d. Dissolve the metals from the electrode by boiling for about twenty minutes

with strong nitric acid in a covered beaker. Remove and wash the electrode, and evaporate the solution to small bulk, to remove most of the acid. Ordinarily, this is best done in an evaporating dish on a water bath. Transfer the concentrated solution to a 100-ml. volumetric flask, and dilute to the mark. Pipet an aliquot part, containing not more than 30 mg. of nickel, into a 400-ml. beaker; add 2 grams of ammonium chloride, dilute to 150 ml., and make just slightly alkaline with ammonium hydroxide. Continue as in I, C, d, above.

III. VOLUMETRIC CYANIDE METHOD ²

A. Application

The following procedure is especially applicable as a routine method for nickel ores, mattes, concentrates, etc. The potassium cyanide titration of nickel gives very satisfactory results and can be carried out in the presence of most of the other elements of the ammonium sulfide group. The reaction may be expressed as follows:



B. Interfering Elements

Few elements interfere in this determination, manganese, copper, lead, silver, arsenic, and antimony being eliminated in the two precipitations described.

If copper is present in amounts not exceeding 0.4 per cent, the copper will replace almost exactly three-quarters of its weight of nickel. If chromium is present, the dark color due to the presence of chromic salts may be obviated by adding to the original sulfuric acid solution a 2 per cent solution of potassium permanganate until a slight permanent precipitate of manganese dioxide is obtained, whereby the chromium is oxidized to chromic acid.

Cobalt counts as nickel. If present, it may be detected during the titration by the darkening of the solution.

C. Procedure

Weigh 0.5 gram of the ore into a 250-ml. beaker, add 15 ml. of nitric acid, heat till red fumes have ceased to come off, add 5 grams

² T. Moore, *Chem. News*, 72, 92, 1895.

of potassium chlorate, and take to complete dryness, but avoid baking. When cool, add 10 ml. of hydrochloric acid and take to dryness as before. Allow to cool, and take up with 10 ml. of hydrochloric acid and 40 ml. of water. Heat gently until all soluble matter has gone into solution, filter, washing thoroughly with successive small amounts of hot water. Make the filtrate alkaline with ammonia, add 10 ml. of bromine water, and boil off the excess of bromine. Filter, redissolve the residue with hydrochloric acid, and reprecipitate to recover any occluded values. Filter through the same filter as before. Acidify the filtrate with hydrochloric acid and add 10 ml. in excess. If manganese is known to be absent, the ammonia precipitation should be omitted, the filtrate from the flask being then ready for the next step. Under either condition, hydrogen sulfide is passed through the hydrochloric acid solution until no further precipitation takes place. Filter, wash thoroughly with hot water, and boil off the excess of hydrogen sulfide from the filtrate. If the solution exceeds 150 ml. in volume, reduce by evaporation. Add 15 ml. of bromine water, to oxidize the solution thoroughly, and boil off the excess of bromine. Cool to approximately 60° F., add 15 ml. of a 10 per cent solution of citric acid, then neutralize with ammonia and add 10 ml. in excess. If any nickel is present the solution will have a distinct blue color, nickel being similar to copper in this respect. The solution is now ready for titration and should be about 200 ml. in volume.

Titrate with the standard cyanide solution until the blue color has disappeared, and add 5 to 10 ml. in excess. It is well to add a round number of milliliters in order that the calculation may be simplified. Add about 10 drops of the potassium iodide indicator, and titrate with the silver nitrate solution until the yellowish cloud appears. If there is any doubt as to the correctness of the end point, add an additional 5 ml. of the cyanide and again finish with the silver nitrate. The results should correspond; that is, if 30 ml. of the cyanide solution had been used and the silver nitrate buret showed a reading of 20 ml., then, if the titration is correct, 35 ml. of the cyanide should take 25 ml. of the silver nitrate, the difference in both titrations being 10 ml. It is this difference between the readings of the two burets that measures the quantity of nickel present,

each milliliter of the difference being equivalent to 0.0025 gram of nickel.

If the cyanide solution is not exactly equal in strength to the silver nitrate solution, the quantity of cyanide used must be calculated to its equivalent in silver nitrate before subtraction is made.

See Chapter XXXIII for the preparation and standardization of the solutions required.

PHOSPHORUS MINERALS

Mineral Name	Chemical Formula	% P ₂ O ₅	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Phosphate rock							
Fluorapatite . . .	3 Ca ₃ P ₂ O ₈ · CaF ₂	42.3	White or tinted	3.2	} Si, Fe, Mn, Ti, Mg, Na, K {	HCl, HNO ₃ HCl, HNO ₃	
Chlorapatite . . .	3 Ca ₃ P ₂ O ₈ · CaCl ₂	41.0	White or tinted	3.2			
Monazite	CeYtPO ₄ · ThO ₂ · SiO ₂	Variable	White or tinted	5.0	Au, Zr, Ca, Mg, Al, B, F, Ti, Sn, Fe, Mn	HCl (difficultly)	Na ₂ CO ₃
Pyromorphite . . .	3 Pb ₃ P ₂ O ₈ · PbCl ₂	15.7	White to yellowish	6.5	As, Ca, Cu, Zn, Fe, Sb, Bi, Cd, V	HNO ₃	
Amblygonite	2 LiF · Al ₂ O ₃ · P ₂ O ₅	47.9	White	3.0	Na, Ca, Mg, K, Si	HCl (difficultly)	Na ₂ CO ₃
Triphylite	Li(FeMn)PO ₄	±45	White to grayish	3.5	Be, Ca, Mg, Al, F, Na, K, Si	HCl	

Phosphorus is of frequent occurrence in the gangue minerals accompanying ore bodies. Most minerals containing phosphorus, such as torbernite, wagnerite, triplite, vivianite, dufrenite, wavelite, autunite, turquois, and reddingite, yield to an attack by hydrochloric or nitric acids. Lazulite, monazite, xenotime, beryllonite, and amblygonite are most easily broken up by alkaline fusion.

Acid decompositions taken to dryness may cause losses of phosphorus, or phosphine, when hydrochloric or sulfuric acids are present; or by the formation of insoluble compounds with elements such as titanium, zirconium, thorium, or tin.

CHAPTER XXII

PHOSPHORUS

I. VOLUMETRIC MOLYBDATE METHOD¹

A. Application

This method is rapid and accurate enough for most technical analyses. It is best applied to low-grade material such as iron ores, pig iron, and limestone. For greater accuracy the gravimetric modification is recommended.

B. Interfering Elements

Arsenic and silica combine with the molybdate reagent to form insoluble compounds. Interference by these elements may be avoided by precipitating the phosphorus at a lower temperature. Excessive amounts of elements that hydrolyze readily, or form relatively insoluble phosphates, may cause trouble; and vanadium, when present, should be reduced to a valence of four.² The precipitation of phosphorus as phosphomolybdate takes place best in solutions containing no other acids than nitric, and all the phosphorus should be present as orthophosphoric acid.

C. Procedure

a. Weigh an amount of the sample containing not more than 40 to 50 mg. of phosphorus. Dissolve, by boiling gently with 20 ml. of hydrochloric and 10 ml. of nitric acid, until the volume is reduced to about 10 ml. Add 20 ml. of nitric acid, and again evaporate to a small volume. Dilute with 10 to 15 ml. of hot water, filter into a 250-ml. flask, and wash with hot water. Dry the residue, and burn off the filter paper by ignition in a platinum crucible. Moisten the cooled residue with a few drops of nitric acid, and add sufficient hydrofluoric acid to dissolve the silica. Evaporate cautiously, just

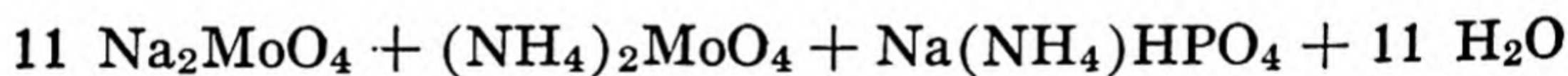
¹ H. Pemberton, *J. Am. Chem. Soc.*, 16, 278, 1894.

² J. R. Cain and F. H. Tucker, *J. Ind. Eng. Chem.*, 5, 647, 1913.

to dryness. Cool, add 2 or 3 grams of sodium carbonate, and fuse the mixture. Dissolve the melt in a little hot water, filter, and wash. Receive the filtrate in the flask with that from the acid decomposition. Neutralize with ammonium hydroxide, and add 3 to 4 ml. of nitric acid and 10 grams of ammonium nitrate. The total bulk should not exceed 50 ml. at this point.

b. Heat to 40-50° C., add 60 ml. of molybdate reagent (see Chapter XXXIII), previously filtered and heated to 40°-50° C., stopper the flask, and shake for five minutes. Allow to stand in a warm place for fifteen minutes, and then filter on a close paper. Wash once with dilute nitric acid and then with a 1 per cent solution of potassium nitrate until free of acid.

c. Place the paper and washed precipitate in the flask in which the precipitation was made. Add a measured amount of standard, carbonate-free, 0.10 *N* sodium hydroxide from a buret until in slight excess, and titrate the excess with 0.10 *N* nitric acid using phenolphthalein as an indicator.



1 ml. of 0.10 *N* NaOH = 0.000135 gram phosphorus

The alkali is best standardized by a standard pulp run parallel to the sample. The preparation and standardization of the solution are described in Chapter XXXIII.

D. Gravimetric Modification

The gravimetric method, though not so rapid as the volumetric, gives more accurate results and can be used on material containing a larger percentage of phosphorus.

a. Proceed as given in I, C, as far as c, or until the washed yellow precipitate is obtained on the paper.

Add 10 ml. of ammonium hydroxide and 20 ml. of water to the flask in which the phosphorus was precipitated, and swirl to dissolve any precipitate adhering to the sides. Heat to boiling, and pour over the bulk of precipitate on the paper, receiving the solution in a 250-ml. beaker. Wash the flask and paper with 2 per cent ammonia; then wash the paper once with 1 : 1 hydrochloric acid and

finally with the ammonia wash solution until the paper is clean and all the precipitate has dissolved. The bulk of solution should be kept under 100 ml.

b. Add hydrochloric acid to the solution until acid. If a precipitate starts to form, clear it by adding ammonium hydroxide drop by drop. Add 1 to 2 ml. of a saturated solution of citric acid and cool. To the cool solution add, dropwise, 10 to 15 ml. of magnesia mixture while stirring, then 10 ml. of ammonium hydroxide slowly with continued agitation. A drop of the solution placed in contact with a drop of ammonium phosphate solution on a black spot plate should give an immediate heavy white precipitate. If necessary add more magnesia mixture. Set aside for four hours or preferably overnight.

c. Filter the precipitate on a close 9-cm. paper, and wash with 2 per cent ammonia wash solution. Dissolve the precipitate adhering to the beaker with dilute hydrochloric acid, and, while heating this acid in the beaker, wash the bulk of the precipitate into a 150-ml. beaker. Place the small beaker under the funnel and dissolve the remainder of the precipitate through the paper with the hot acid. Wash the paper with 1 : 1 hydrochloric acid and hot water.

Cool the filtrate, add 2 ml. of magnesia mixture, and then ammonium hydroxide slowly as before with constant stirring until the ammonia is in 10 per cent excess. Let stand for 2 hours, and filter through the same paper, washing well with dilute ammonia.

d. Transfer the paper and precipitate to a No. 00 porcelain crucible, dry, char, and ignite at about 1000° C. until the residue is white. Cool and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$ containing 27.86 per cent phosphorus or 63.79 per cent P_2O_5 . Refer to **Chapter XXXIII** for the preparation of the magnesia mixture.

II. SHORT GRAVIMETRIC METHOD³

A. Application

The method is applicable to phosphate rock, superphosphate, and similar materials. It is recommended for use in standardization and umpire analyses of phosphate rocks and similar materials, but

³ J. I. Hoffman and G. E. F. Lundell, *Nat. Bur. Standards J. Research*, 19, 59, 1937, by permission of Dr. Lundell.

is not sufficiently rapid to replace the usual volumetric method employed in routine analyses.

B. Interfering Elements

Iron, aluminum, titanium, silica, calcium, zinc, manganese, fluorine, and organic matter in the percentages found in phosphate rock do not interfere. Sulfates and nitrates, which might be introduced in the manufacture and mixing of fertilizers, likewise do not interfere.

C. Procedure

a. Transfer 0.5 gram of the dried material to a 300 ml. Erlenmeyer flask, and add 15 ml. of hydrochloric acid and 3 ml. of nitric acid. Place a small watch glass over the mouth of the flask, and boil gently for thirty minutes.

b. Rinse and remove the watch glass, and, without filtering, add 30 grams of ammonium citrate, 10 ml. of hydrochloric acid, and 100 ml. of magnesia mixture. Neutralize the solution with ammonium hydroxide, using litmus paper as indicator, and add 3 ml. of ammonium hydroxide in excess. Dilute the solution to 225 to 250 ml. with water, add a few glass beads, stopper the flask tightly, shake on a shaking machine for about one-half hour, and allow to stand overnight. Filter through a paper of close texture, and wash the flask and paper once with a small quantity of diluted ammonium hydroxide. Discard the filtrate.

c. Dissolve any magnesium ammonium phosphate remaining in the flask in about 50 ml. of warm diluted hydrochloric acid (1 : 4), and pour the solution through the paper to dissolve the phosphate that was transferred to the filter, and to separate any insoluble residue that may have remained from the decomposition. Wash the paper and flask with more of the same acid, and add 0.3 gram of citric acid and 1 ml. of magnesia mixture to the solution, which should have a volume of about 100 ml. While stirring, add ammonium hydroxide until the solution is alkaline to litmus, and then add 5 ml. in excess. Stir occasionally during one-half hour, and allow to stand for 4 hours.

d. Collect the precipitate on a 9-cm. paper of close texture, wash with cool diluted ammonium hydroxide, and transfer the paper and

precipitate to a porcelain crucible. Char the paper without flaming, burn off the carbon below 900° C., and finally ignite to constant weight, preferably in a muffle, at 1050° to 1100° C. The weight of the magnesium pyrophosphate, multiplied by 63.79 and divided by the weight of the sample, yields percentage of P_2O_5 in the sample.

Tests at the Bureau of Standards have shown that the time of standing in the first precipitation can be reduced to three hours and in the second to two hours, if the solutions are chilled before shaking or stirring and then allowed to stand in ice water or in a refrigerator at 5° to 10° C. With small quantities (less than 10 mg. of P_2O_5), the longer time of standing is essential, and even then it is best to chill and shake alternately two or three times.

POTASSIUM AND SODIUM MINERALS

Mineral Name	Chemical Formula	% K ₂ O	% Na ₂ O	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
							Acid	Flux
Sylvite.....	KCl	63.2	Pink to white	2.0	Na, Ca, Mg, H ₂ O, Fe, Si, S	H ₂ O soluble	
Polyhalite....	K ₂ SO ₄ ·2 CaSO ₄ ·MgSO ₄ ·2 H ₂ O	15.6	Pink to white or gray	2.8	Same	Same	
Carnallite....	KCl·MgCl ₂ ·6 H ₂ O	16.9	White to pink or brown	1.6	Same	Same	
Kainite.....	KCl·MgSO ₄ ·3 H ₂ O	18.9	White to pink or brown	2.1	Same	Same	
Langbeinite....	K ₂ SO ₄ ·2 MgSO ₄	22.7	White to gray	2.8	Same	Same	
Orthoclase....	K ₂ O·Al ₂ O ₃ ·6 SiO ₂	16.9	White	2.6	Fe, Mn, Ca, Mg, Na	HF+HCl	CaCO ₃ +NH ₄ Cl
Carnotite.....	K ₂ O·2 UO ₃ ·V ₂ O ₆ ·nH ₂ O	5 to 7	Lemon-yellow	4.0	Si, Ca, Mg, Fe	HCl	
Halite.....	NaCl	53.0	White, gray or tinted	2.2	K, Ca, Mg, H ₂ O, Fe, Si, S	H ₂ O soluble	
Soda niter....	NaNO ₃	36.5	White to yellow, gray or tan	2.2	S, Cl, K, Ca, Mg, Si, I	Same	
Thenardite....	Na ₂ SO ₄	56.3	White to brownish	2.7	Cl, N, C, Ca, Mg, K	Same	
Gaylussite....	Na ₂ CO ₃ ·CaCO ₃ ·5 H ₂ O	20.9	White to gray	1.9	K, Mg, S, Cl	Acid soluble	
Borax.....	Na ₂ O·2 B ₂ O ₃ ·10 H ₂ O	16.2	White	1.7	K, Ca, Mg, Si	H ₂ O soluble	
Cryolite.....	Na ₃ AlF ₆	32.8	White	3.0	Fe, Mn, Si	H ₂ SO ₄	
Albite.....	Na ₂ O·Al ₂ O ₃ ·6 SiO ₂	11.8	White	2.6	Fe, Mn, Ca, Mg, K	CaCO ₃ +NH ₄ Cl
Mirabilite....	Na ₂ SO ₄ ·10 H ₂ O	19.3	White	1.5	K, Ca, Mg, Fe, Si	H ₂ O soluble	

Sodium and potassium are practically always present to greater or less extent in the gangue minerals of other ores. These silicates of the alkalis are usually in combination with calcium, magnesium, or aluminum, and are best broken up by the J. Lawrence Smith method.

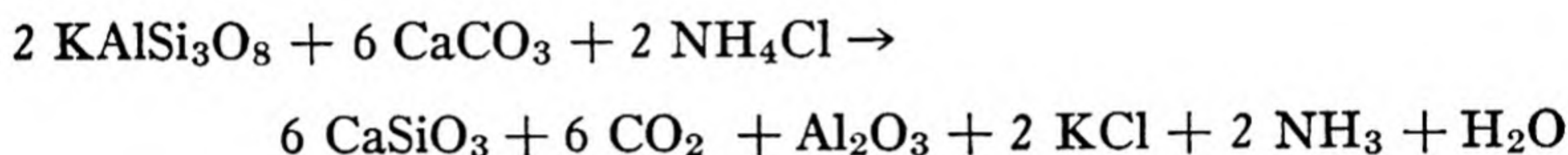
CHAPTER XXIII

POTASSIUM AND SODIUM

I. J. LAWRENCE SMITH METHOD¹

A. Application

This method and the hydrofluoric acid method are widely used for the decomposition of silicates preparatory to the determination of the alkalies. By this means the alkalies are obtained in the form of chlorides; the remaining metals are for the most part left behind as oxides, and the silica is changed to calcium silicate, as represented by the following equation:



The alkali chlorides together with the calcium chloride can be removed from the sintered mass by leaching with water, the other constituents remaining undissolved.

B. Interfering Elements

The most common interference encountered is that of soluble sulfates, either present in the original material or formed from sulfides during the decomposition. Magnesium interferes when present in appreciable amounts owing to the solubility of its carbonate. Zinc and molybdenum are occasionally interfering elements and are best removed by precipitation with hydrogen sulfide from the mixed chloride solution. Less frequently, fluorine, boron, thallium, selenium, or tellurium may be present in sufficient amount to cause trouble.

C. Procedure

a. Mix 0.5 gram of the finely ground mineral with 0.5 gram of sublimed ammonium chloride, by trituration in an agate mortar;

¹ *Am. J. Sci.*, (2) 50, 269, 1871.

then add 3 grams of calcium carbonate and mix intimately with the rest. Transfer to a platinum crucible with the help of glazed paper. The crucible should be lined on the inside with a thin even coat of calcium carbonate by pressing the form used for straightening the crucible firmly down on a small amount of calcium carbonate placed on the bottom. See Fig. 14. Scrub the mortar with 1 gram of calcium carbonate, and add the scrubbings to the main portion in the crucible.

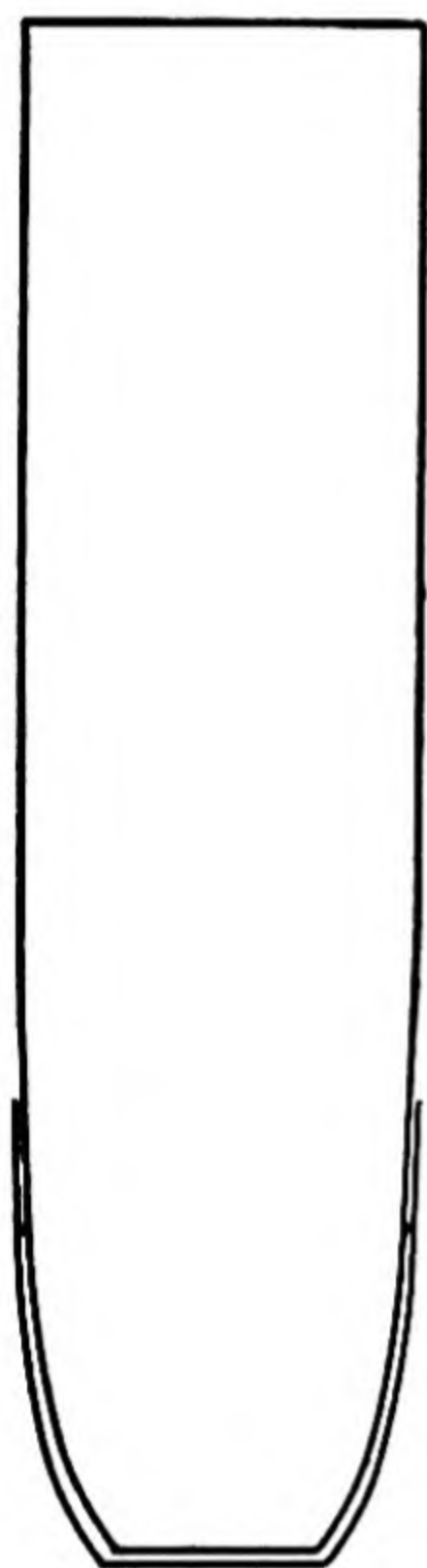


FIG. 14.

The apparatus used for the determination of mercury (Mercury, II, C) will work very well for this method by simply setting the asbestos ring over a Gilmer or similar heater.

If a Smith crucible is used it is placed in a slightly inclined position for heating. This is best done by inserting the covered crucible through a hole in the side of a fire-clay cylinder, such as a large crucible with the bottom cut away. The top of the platinum crucible projects from the side and is thus protected from the flame. Heat gradually over a small flame until no more ammonia is evolved.² This should take about fifteen minutes. Now increase the heat until finally the lower three-fourths (and no more) of the crucible is brought to a dull red. Maintain this temperature for fifty or sixty minutes. After cooling, the sintered cake can usually be removed by gently

tapping the inverted crucible. If it should not come out easily, add a little water and warm gently for a few minutes to soften the cake; then wash it into a large porcelain or, better, platinum dish. Add 50-75 ml. of hot water and heat the covered dish for half an hour, replacing the water lost by evaporation. Reduce the large particles to fine powder by rubbing with a pestle in the dish. Finally, decant the clear solution through a filter, wash the residue four times with a hot saturated solution of limewater by decantation; then transfer to the filter and wash with the hot limewater until a few milliliters

² During this part of the operation the heat should be kept so low that ammonium chloride does not escape. It is dissociated into ammonia and hydrochloric acid by the heat, and the acid unites with the calcium carbonate to form calcium chloride. (Treadwell, Hall, Analytical Chemistry, Vol. II.)

of the washings give only a slight turbidity with silver nitrate. To make sure that the decomposition of the mineral has been complete, treat the residue with a little hydrochloric acid. It should dissolve completely.

With either crucible, actual fusion of the mass should not occur. The CaCl_2 formed by the reaction between the NH_4Cl and the CaCO_3 attains a state of fusion and is absorbed by the large excess of CaCO_3 present. Actual fusion of the silicate would render subsequent disintegration of the mass impossible. If fusion of the mass occurs in spite of the low temperature maintained, it may be due to the fusible nature of certain silicates, notably those containing much ferrous iron. If this happens it is better to begin anew and increase the proportion of CaCO_3 to 8-10 parts.

Treat the aqueous solution with ammonia and ammonium carbonate, heat, and filter. The precipitate retains small amounts of alkali. Dissolve it in hydrochloric acid, and repeat the precipitation with ammonia and ammonium carbonate. Combine the filtrates and evaporate to dryness in a porcelain or platinum dish. While the major portion is evaporating, transfer it in portions to a smaller dish, where the evaporation is continued, finally rinsing all into the small dish. When the final dry residue is obtained in the small dish, cover the dish and heat it for a while in a drying-oven at 110°C . This lessens the danger of subsequent loss by decrepitation. Now expel the ammonium salts by careful ignition over a moving flame. Allow to cool, dissolve the residue in a little water, and test a small drop of the solution on a black spot plate with a drop of barium chloride solution. If sulfates are present, enough barium chloride solution is added to the dissolved residue to precipitate all of the sulfate ion completely, and the barium sulfate is filtered off on a small paper and washed well with hot water. The excess barium in the solution is removed by heating with a little ammonia and ammonium carbonate again. Filter off the barium carbonate on a small paper and wash with hot water. Heat the filtrate and add a little ammonia and ammonium oxalate to remove the last traces of calcium. After it has stood for twelve hours, filter off the calcium oxalate, receiving the filtrate in a weighed platinum dish. Evaporate it to dryness, cover it, and heat it, still covered, in an oven at 110°C .; then ignite gently to expel ammonium salts. Cool, moisten with hydrochloric

acid to convert any carbonate into chloride, and then repeat the evaporation and ignition with the same precautions as before. Determine the weight of the contents of the dish, which represents the amount of alkali chloride present. To determine potassium, dissolve the residue in a little water and precipitate as described in b or c.

b. To the aqueous solution as chlorides in a platinum or porcelain evaporating dish (the weight of the mixed chlorides being known), add a slight excess of hydrochloroplatinic acid (H_2PtCl_6) and evaporate to dryness on a water bath. The drying is to dehydrate the sodium platonic chloride and render it more soluble in alcohol. It is a good plan to have the platinum solution contain 10 per cent of platinum, i.e., 1 gram in every 10 ml., and, in order to use the right quantity and avoid unnecessary excess, make the following calculation:

Assume that the mixed chlorides consist entirely of NaCl. Call their weight a . Then from the formula $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ we find that 46 parts of Na require 195.2 parts of Pt. Since 46 parts of Na correspond to 116.92 parts of NaCl, we have the proportion

$$116.92 : 195.2 = a : \text{Pt required}$$

Solving this and multiplying the result by 10, we arrive at the number of milliliters of platinum solution required. Always add 0.3-0.4 ml. in excess.

It is necessary to convert all the sodium, as well as the potassium, to the platinum compound, as otherwise the undecomposed sodium chloride, being insoluble in absolute alcohol, would contaminate the potassium platonic chloride; the calculation is therefore made as above. After the evaporation, add to the cool residue a few milliliters of absolute alcohol (methyl alcohol is the best) and thoroughly disintegrate the solid mass with a stirring-rod or platinum spatula. Decant the clear liquid through a filter moistened with alcohol, and then repeat the stirring with fresh portions of alcohol until a perfectly colorless filtrate is obtained and the remaining salt in the dish is pure golden-yellow with no intermixed orange-colored particles of Na_2PtCl_6 . That compound is soluble in the alcohol; the corresponding potassium salt is not. Transfer the washed residue to the filter, allow to drain completely, and then dry

in an air bath at 80°-90° C. When dry, carefully transfer as much of the precipitate as possible to a watch glass. Replace the filter in the funnel, and dissolve the adhering precipitate (and also any in the original dish) by washing with a little hot water, receiving the filtrate in a weighed platinum dish or crucible. Evaporate the solution to dryness at a low temperature on the water bath, and then add the precipitate on the watch glass. Dry the whole at 160° C., and weigh as K_2PtCl_6 . Multiply this weight by 0.30561 to obtain that of the KCl. Although this factor is correct according to the less recent values of the atomic weights, the factor 0.30671 is the correct one according to the latest values. This figure, however, does not actually give results so near to the truth as the older factor. This is because our assumption as to the formula K_2PtCl_6 is not quite correct. Changes are produced by the evaporation which are compensated for by the use of the old factor.

The weight of the KCl in the mixed chlorides having been determined, the difference from the total weight is the NaCl.

Multiply the weight of the KCl by 0.63173 to obtain the weight of the K_2O .

Multiply the weight of the NaCl by 0.53028 to obtain the weight of the Na_2O .

c. To the weighed mixed chlorides add just enough water to dissolve the salts, then 5 ml., or more, of 20 per cent perchloric acid, and evaporate to dryness on a hot plate and until all fumes of perchloric acid have disappeared. If the heavy fumes fail to appear, cool, again take up in a little water, add 5 ml. more of perchloric acid, and repeat the evaporation. Two evaporations, each showing the heavy fumes, are necessary, the fumes being entirely expelled each time.

Allow to become completely cold, then add 25 ml. of a saturated solution of potassium perchlorate in 95 per cent grain alcohol (or denatured alcohol). Cover the dish and allow a little time for the soluble perchlorates to dissolve. The final salts consist of the perchlorates of the bases present, of which only potassium perchlorate is insoluble in the alcohol, mixed perhaps with barium sulfate and small amounts of organic and other insoluble matter.

Prepare a Gooch crucible with a thick asbestos mat, and have it dry. Thoroughly loosen up the salts in the dish with a rubber-

tipped glass rod, rubbing the particles so as to leave only a powdery residue, free from lumps. Rub a little grease on the lower side of the lip of the dish, as the alcohol has a tendency to run down the outside, and filter through the Gooch (not yet weighed). Using the alcoholic perchlorate solution in a small wash bottle, transfer all the residue from the dish to the filter, allow all the liquid to run through, and then wash six times with the alcoholic perchlorate solution, allowing to drain completely each time. Finally, drain thoroughly and then dry in an oven at 130° - 150° C., cool and weigh. Now wash the residue in the Gooch six times with hot water, which will dissolve the potassium perchlorate, then twice with alcohol, and once with a very little of the alcoholic perchlorate solution. Drain completely, dry, cool, and weigh as before. The loss in weight represents the potassium perchlorate. Multiply this by 0.3399 to obtain the K_2O .

The alcoholic perchlorate solution is made by simply shaking up an excess of potassium perchlorate with the alcohol, allowing to stand some time, best overnight, and always shaking the mixture and filtering or decanting a portion so as to have the solution saturated at the laboratory temperature when used.

D. Modification

In the official method of the Association of Official Agricultural Chemists, the procedure, after the filtrate from the disintegrated sintered mass has been obtained, is as follows:

Precipitate the calcium with ammonia and ammonium carbonate, allow to settle, and then concentrate the supernatant solution, decanting in portions if necessary, in a small porcelain or platinum dish, finally rinsing in the precipitate. When the whole is thus reduced in the small dish to about 30 ml., add a little more ammonia and ammonium carbonate. Evaporate to dryness on a water bath, expel the ammonium chloride by gentle ignition, and dissolve the residual alkali chlorides in 3-5 ml. of water.

A little black or dark brown flocculent matter usually remains undissolved, and the solution may still contain traces of calcium. Add 2 or 3 drops of ammonia and ammonium carbonate, warm gently, and filter through a very small filter into an unweighed but weighable platinum dish. Evaporate to dryness on a water bath,

heat at dull red to incipient fusion of the alkali chlorides, and, after cooling, weigh. Dissolve the mixed chlorides in a little water and filter through a small filter into a porcelain dish. Ignite the filter in the platinum dish previously used, and weigh. Subtract this weight from the first weight to obtain the weight of the $\text{NaCl} + \text{KCl}$.

Determine the K_2O in the filtrate in the porcelain dish by precipitating with platinum chloride (b), adding sufficient platinum chloride to combine with the total weight of alkali chlorides calculated as NaCl , i.e., an amount of metallic platinum 1.67 times the weight of alkali chlorides found.

II. HYDROFLUORIC ACID METHOD³

A. Application

Same as preceding method.

B. Interfering Elements

The interferences are similar to those of the J. Lawrence Smith method, which is usually to be preferred, especially with material high in magnesium.

C. Procedure

Treat 1 gram of the finely powdered silicate in a platinum dish with pure strong sulfuric and hydrofluoric acids until decomposition is complete. It is best to add the sulfuric acid first, to prevent spattering, and then to add about an equal amount of hydrofluoric acid and warm gently. Finally, evaporate to dryness on the water bath.

Dissolve the residue in hot water, add 5 ml. of a saturated solution of barium hydroxide, and heat to boiling. Allow to settle a short time, and then test the clear liquid with a little more barium hydroxide solution, to be certain that enough has been added. When the precipitation is complete, filter and wash well with hot water. Heat the filtrate to boiling, and add a little ammonia and ammonium carbonate to complete the precipitation of calcium, barium, etc., and, after allowing to stand a short time on the water bath, filter and wash the precipitate thoroughly with hot water.

Evaporate the filtrate to dryness in platinum or porcelain and then expel the ammonium salts by a heat just below redness. Take up the cool residue in a little hot water; add a few drops of ammonia,

³ J. J. Berzelius, *Pogg. Ann.*, 1, 169, 1824.

a drop or two of strong ammonium carbonate solution, and a few drops of ammonium oxalate solution. After allowing to stand a short time on the water bath, set aside for a few hours and then filter, washing with hot water.

Evaporate the filtrate to dryness on the water bath, and heat the residue to dull redness until all ammonium salts are expelled and it has become nearly or quite white. Cool, dissolve in a very small amount of water, and filter into a weighed platinum dish. Add a few drops of hydrochloric acid and evaporate to dryness on the water bath. Heat the residue to dull redness, cool in a desiccator, and weigh as mixed potassium and sodium chlorides. Repeat the heating until a constant weight is obtained. Dissolve the chlorides in a small amount of water. If a residue remains undissolved, the separation must be repeated until the chlorides finally obtained are entirely soluble.

Proceed with the solution of the chlorides as in I, C, b or c.

III. SHERRILL POTASH METHOD ⁴

A. Application

The following procedure is rapid and accurate for the determination of potash in all grades of water-soluble material such as fertilizer salts and reagents. The method is based on the precipitation of potassium with sodium cobaltinitrite under controlled conditions. The resulting precipitate is settled rapidly in a centrifuge and its volume compared with that of a standard similarly treated.

B. Interfering Elements

Ammonium salts react with this reagent to form a precipitate similar to that of the potassium. None of the other water-soluble salts commonly present interfere.

C. Special Solutions

a. *Standard Potassium Chloride Solution.* Dissolve 15.835 grams of dried, pure KCl in distilled water, add 25 drops of glacial acetic acid, and dilute to exactly one liter.

One milliliter is equal to 0.01 gram K_2O .

⁴ Method of the Potash Company of America, Carlsbad, New Mexico, adapted from the procedure of E. Sherrill, *J. Ind. Eng. Chem.*, 13, 227, 1921.

b. Sodium Cobaltinitrite Stock Solution. Dissolve 250 grams of cobalt acetate ($\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$) in 800 ml. of distilled water. In another beaker dissolve 450 grams of sodium nitrite in 800 ml. of distilled water. Add the solution of cobalt acetate to the solution of sodium nitrite, with stirring, and dilute to 2 liters. Allow to age at least twenty-four hours before using. This solution will keep for about two months.

c. Sodium Cobaltinitrite Precipitating Solution. Mix 100 ml. of the stock solution with 65 ml. of distilled water and 5 ml. of glacial acetic acid in a liter bell flask. Cork, and allow to stand overnight. This solution does not keep more than twenty-four hours and should be left in a cool place when not in use.

D. Procedure

a. The weight of sample taken is judged by the K_2O content. If the approximate content is unknown, a trial analysis is made with a 5-gram sample. From the result obtained the correct weight for the final analysis may be determined from the accompanying table. The weights in this table represent the volume of the dissolved sample divided by the percentage of K_2O in the sample.

% K_2O	Grams/200 ml.	% K_2O	Grams/200 ml.	% K_2O	Grams/200 ml.
5	40.0	25	8.00	45	4.44
6	33.3	26	7.70	46	4.35
7	28.6	27	7.40	47	4.25
8	25.0	28	7.14	48	4.17
9	22.2	29	6.90	49	4.08
10	20.0	30	6.67	50	4.00
11	18.2	31	6.46	51	3.92
12	16.6	32	6.25	52	3.85
13	15.4	33	6.00	53	3.77
14	14.3	34	5.88	54	3.70
15	13.3	35	5.72	55	3.64
16	12.5	36	5.56	56	3.58
17	11.8	37	5.40	57	3.51
18	11.1	38	5.26	58	3.45
19	10.5	39	5.13	59	3.39
20	10.0	40	5.00	60	3.33
21	9.53	41	4.88	61	3.28
22	9.10	42	4.76	62	3.23
23	8.70	43	4.65	63	3.18
24	8.34	44	4.54		

b. The weighed sample is placed in a 200-ml. volumetric Kohlrausch sugar flask and dissolved carefully with water, agitating the flask to prevent the formation of lumps, which do not readily dissolve. Five drops of glacial acetic acid are added, and, after diluting to volume, and mixing, the solution is filtered into a 400-ml. beaker using an 8-inch qualitative filter paper in a stemless sugar funnel placed directly on the top of the beaker.

c. The sodium cobaltinitrite precipitating solution is warmed slowly to 80° F. and 17.6 ml. pipeted (using a Babcock milk pipet) into each of two Sherrill potash tubes (Fig. 15). To the first tube is added exactly 5 ml. of the standard KCl solution, by means of a pipet, and to the second tube exactly 5 ml. of the solution being analyzed. The pipeting of these solutions must be done as accurately as possible, as one drop will seriously affect the results on high-grade material.



FIG. 15.

d. The yellow precipitates of potassium cobaltinitrite formed are given about five minutes to crystallize and settle down in the tubes, and are then centrifuged for one minute at 1200 r.p.m. The top of the precipitate in each tube is then leveled by gently tapping on the side, and the tubes replaced in the centrifuge, 180 degrees reversed from their original position in the trunnion shields, and again revolved at the same speed for fifteen seconds.

e. The volume of precipitate in each tube is then read and recorded. The volume of the standard should be close to a reading of 10 on the tube, or the test must be repeated. If the standard reads above 10, the precipitating solution should be raised a few degrees in temperature; if below 10, it should be cooled. When the proper temperature is attained no difficulty will be encountered in obtaining a reading within one division of 10 for the standard in succeeding determinations. If the volume of the unknown is more than five divisions higher or lower than that of the standard, the weight of sample should be recalculated and the test repeated. Best results are obtained when the volumes of the standard and unknown are close to each other in value or close to 10 on the scale.

$$\% \text{K}_2\text{O} = \frac{\text{Volume of unknown} \times 100}{\text{Volume of standard} \times \text{grams of sample per 100 ml.}}$$

Multiply the percentage of K_2O by 1.5835 to obtain the percentage of KCl .

f. The accuracy of this method depends on treating the standard and unknown solutions in exactly the same manner. The solutions should be at the same temperature, preferably at about 70° to 75° F. and the operations performed in a warm laboratory. The precipitate must be given time to crystallize and settle properly, to allow air bubbles to rise, and to prevent the precipitate from packing above the narrow graduated part of the Sherrill tubes. The few drops of acetic acid are added to keep the sodium from precipitating, and to prevent the precipitate from adhering to the sides of the tube, which must be kept clean at all times. The volumes of the precipitates of the standard and the sample should be nearly equal owing to the differences in density of the precipitate at different heights in the tube. Upon centrifuging, the precipitate is packed more tightly at the bottom of the tube than the top.

The Sherrill potash tubes may be readily cleaned after use by means of a fine jet of water from a $3\frac{1}{2}$ -inch veterinary hypodermic needle connected by a rubber tube to the water faucet.

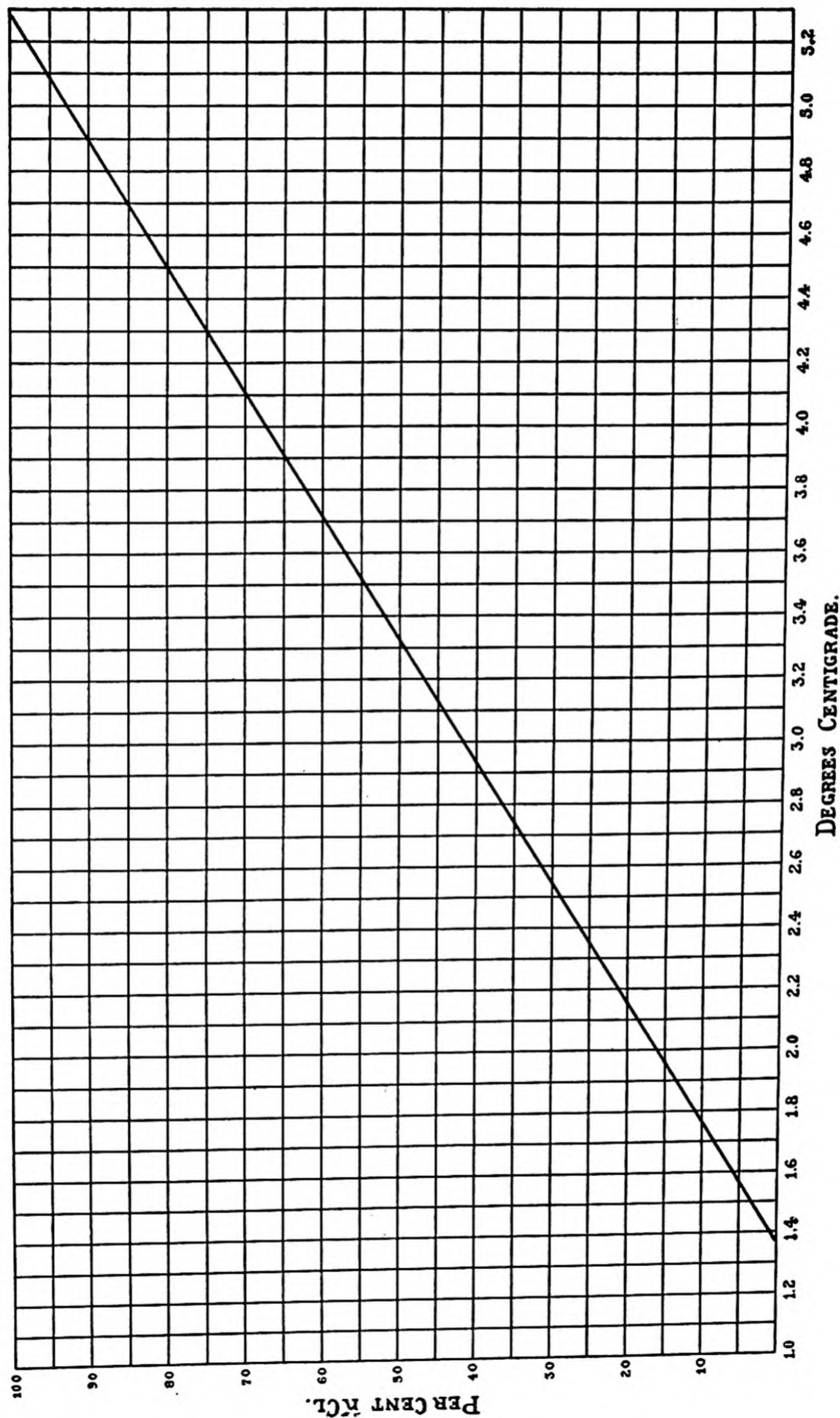
IV. RAPID METHOD FOR THE ESTIMATION OF KCl IN $\text{KCl} + \text{NaCl}$ MIXTURES⁵

This method is based on the fact that a mixture of KCl and NaCl added to water causes a drop in temperature of the resulting solution corresponding in degree to the percentage content of the two salts.

Apparatus. The apparatus used for the determinations consists of a wide-neck Thermos flask mounted on a variable-speed turntable and arranged so that a Beckmann differential thermometer (reading to 0.01 degree Centigrade over a range of $5\frac{1}{2}$ degrees) can be lowered or raised in or out of the flask. The revolving flask allows just enough agitation to aid solution of the salts and to bring the liquid to an even temperature throughout.

Method. Two hundred milliliters water at approximately 22° C. is measured in a graduate and transferred to the flask, where it is

⁵ A. J. Weinig, unpublished.



allowed to revolve slowly about the thermometer, while the 20-gram sample of salt mixture is being weighed. The weighed sample is placed on a sheet of paper and transferred to the flask after the temperature of the thermometer is carefully recorded. Care must be taken that the salt mixture is dropped into the water and does not adhere to the side of the flask. The mercury is then allowed to drop till it reaches a permanent low level, and the resulting temperature is recorded. From the difference in the two readings (the drop in temperature), the percentage of KCl or NaCl may be found on the chart.

Remarks. Pure crystalline KCl-NaCl mixtures give excellent results with no difficulty in operation. Impure salt mixtures tend to give inaccurate results. Tailings samples, low in KCl content and containing appreciable amounts of impurities, dissolve very slowly and, if allowed time enough to dissolve of their own accord, give high results. This may be overcome by stirring the mixture with a glass rod and policeman until the mercury drops no lower on continued stirring for 30 seconds.

The stirring must be done below the surface of the liquid, as beating air into the liquid or too vigorous agitation gives rise to errors. Stirring is necessary on all finely ground or soapy samples but should be avoided as much as possible. With a little practice, the operator can judge the correct amount and time for individual samples to be stirred.

Samples which are contaminated with soap and tend to froth may be settled by the addition of a few drops of fuel oil.

In mixtures high in KCl content, the mercury will drop very rapidly and then rise again about a tenth of a degree before reaching a definite level for the second reading.

SILICATE MINERALS

Mineral Name	Chemical Formula	% SiO ₂	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Beryl.....	3 BeO·Al ₂ O ₃ ·6 SiO ₂	67.0	White or tinted	2.7	Fe, Mn, Ca, Li	Insol.	Na ₂ CO ₃ , NaOH
Phenacite.....	2 BeO·SiO ₂	54.5	White or tinted	3.0	Same	Insol.	Na ₂ CO ₃ , NaOH
Garnierite.....	H(NiMg)SiO ₄ ·nH ₂ O	Variable	Greenish white	2.3 to 2.8	Cr, Fe, Co, Al	HCl	NaOH
Calamine.....	2 ZnO·SiO ₂ ·H ₂ O	25.0	White	3.5	Fe, Pb, Cu, Ca, Mn	HCl (partly)	Na ₂ CO ₃
Willemite.....	2 ZnO·SiO ₂	27.0	White to gray	4.0	Mn, Fe, Ca, Pb, Cu	HCl (partly)	Na ₂ CO ₃
Zircon.....	ZrO ₂ ·SiO ₂	32.8	White	4.7	Fe, Au, Sn, Pt, Ca, Al, Na, K, W	Insol.	Na ₂ CO ₃ , KHSO ₄
Chrysocolla.....	CuO·SiO ₂ ·2 H ₂ O	34.3	White to bluish green	2.2	Al, Fe, Mn, Pb, Zn, Au, Ag	HNO ₃	Na ₂ CO ₃
Kaolinite.....	2 SiO ₂ ·Al ₂ O ₃ ·2 H ₂ O	46.5	White to gray or tinted	2.6	Fe, Ti, Ca, Mg, P, S, Mn	Insol.	Na ₂ CO ₃ , KHSO ₄
Monazite.....	CeYtPO ₄ ·ThO ₂ ·SiO ₂	Variable	White or tinted	5.0	Au, Zr, Ca, Mg, Al, B, F, Ti, Sn, Fe, Mn	HCl (difficultly)	Na ₂ CO ₃
Roscoelite.....	K, Al, V, H ₂ O silicate	Variable	White, micaceous	3.0	Fe, Mn, Ca, Mg, Na	Insol.	Na ₂ CO ₃

Silicon is nearly always present in ore analysis and often causes high results in analyses for other elements. It is a major constituent of a great many minerals used for industrial purposes, such as refractories, glass sand, abrasives, asbestos, cement, ceramic materials, mineral fillers, foundry sand, building stone, insulating materials, mica, and talc.

CHAPTER XXIV

SILICON

I. INSOLUBLE RESIDUE OR "SILICA"

A. Application

In the valuation of ores, it is often customary to designate as "silica" the insoluble residue remaining after certain conventional treatments with acids. Precautions are taken to remove lead compounds, and sometimes other efforts at purification are made, so that the final insoluble residue, or so-called silica, shall consist mainly either of fairly pure silica or a mixture of silica and undecomposed silicates.

B. Interfering Elements

Various elements form difficultly soluble salts according to the method of decomposition, requiring the judgment of the analyst as to the necessary treatment. The most common interferences include silver chloride, lead chloride and sulfate, barium sulfate, and tungstic acid. Less frequently encountered may be: columbic, tantalic, boric, molybdic, vanadic, antimonie, and stannic acids; the difficultly soluble sulfates of aluminum, chromium, nickel, and iron; and the phosphates of titanium, zirconium, and thorium. Potassium may cause trouble as the perchlorate, and antimony as the oxychloride. Fluorine is always a serious interfering element owing to the volatilization of silica as silicon tetrafluoride.

C. Procedure

The methods followed in the different laboratories may differ somewhat in unimportant details, but in general are as follows:

Unless there is some special reason for doing otherwise, 0.5 gram is always taken for the determination.

a. *Sulfides*. Treat in No. 0 beaker, or small casserole, with strong nitric acid, 7-10 ml. Heat gently until strong action has ceased. Evaporate to dryness and bake until free from acid. Cool,

add about 20 ml. hydrochloric acid (1 part acid and 1 part water), and heat until solution is as complete as possible. Filter, wash first with hot dilute hydrochloric acid, then hot water. Ignite and weigh.

Occasionally some ores high in zinc or lead sulfide may be treated to advantage, first with hydrochloric acid, and then as above, but the result should be the same by either method properly carried out.

b. *Oxidized Ores in General.* Treat with strong hydrochloric acid, 7-10 ml. Boil until dissolved; add a little nitric acid (0.5 ml. is usually plenty); evaporate to dryness, and bake to the complete expulsion of acid fumes. Cool, take up with hydrochloric acid, and proceed as with sulfides.

With some ores containing carbonaceous matter, it may be necessary to bake for a long time, as such residues often hold acid very tenaciously.

c. *Manganese Oxides.* Nitric acid is omitted entirely with these.

d. *Lead Oxide Ores.* Some of these usually yield gelatinous silica and must be carefully dehydrated at a temperature which is not too high.

Care must be taken to insure the removal of all lead salts from the insoluble residue. If filtrations are conducted rapidly and with hot solutions, washing with hot dilute hydrochloric acid is perfectly safe. However, washing with hot ammonium chloride or acetate solution is often practiced, and there is no objection to it. This removal of lead needs special care in barium sulfate ores, which seem to render the complete solution of the lead salts more difficult.

e. *Oxidized Material Which Has Been Strongly Ignited.* Digest with hydrochloric acid without boiling at first, then evaporate nearly to dryness, add a few drops of nitric acid, and evaporate to complete dryness. Occasionally it may be necessary to repeat this treatment, this being a matter of individual judgment. Finally, bake to complete expulsion of acid and proceed as before.

f. *Roasted Ores, Acid Works' Residues, etc.* Digest with hydrochloric acid, without boiling, until oxidized portion is dissolved, add 2-3 ml. of nitric acid, boil to decompose sulfides, evaporate to dryness, and proceed as before.

g. *Ores or Products Containing Magnetite.* Some mixed oxidized and sulfide ores, and also often furnace mattes, contain magnetite.

When this is known or suspected the material is treated as above under "Roasted Ores, etc.," except that nitric acid in larger quantity may sometimes be necessary.

h. Barium Sulfate Ores. Treat with 10 ml. hydrochloric acid (1 part acid and 1 part water), boil a few minutes, add 4-5 ml. nitric acid, and after action has ceased evaporate to dryness. Bake and proceed as usual.

After total insoluble is weighed, fuse with sodium carbonate or mixed carbonates, digest the melt with water until disintegrated, filter and wash. Wash out the fusion crucible with 3-5 ml. hydrochloric acid (1 : 1), and with this dissolve the residue on the filter, being careful that all the residue is dissolved and the filter washed clean. Precipitate the barium in boiling solution with a slight excess of dilute sulfuric acid, and allow to stand at least two hours before filtering. The barium sulfate so obtained is deducted from the total insoluble residue.

i. High-grade Silver or Tungsten Ores. Leach the filtered and washed insoluble residue with hot dilute ammonia before igniting and weighing.

j. Fluorspar.¹ Digest the finely pulverized sample in a 150-ml. beaker with 15 ml. of 20 per cent perchloric acid saturated with boric acid at 50° C. until copious fumes have been evolved for about five minutes. Add a few milliliters of water and repeat the fuming for five minutes more. Dilute to 75 ml., heat, filter, and wash the residue with hot water. Ignite and weigh.

k. Ores and Slags That Gelatinize with Acids. Some ores and furnace products are more or less completely decomposed by acids with the formation of gelatinous silica. Slag that has been suddenly chilled by dipping an iron bar into the molten mass, and then plunging it with the adhering slag into cold water, may usually be entirely decomposed by acids. Roasted ores generally give gelatinous silica. If such substances are treated in the usual way, the gelatinous silica is likely to form a cake which adheres to the bottom of the beaker and greatly hinders decomposition by surrounding particles of the ore with a more or less impervious coating. Material of this class may be treated as follows:

¹ W. T. Schrenk and W. H. Ode, paper presented at the 77th meeting of the American Chemical Society, Columbus, Ohio, 1929.

Moisten the 0.5 gram of substance in the beaker (a 4-inch porcelain casserole or dish is better) with 2 or 3 ml. of water, and then add gradually about 10 ml. of strong hydrochloric acid, stirring or shaking the mixture at the same time to prevent coagulation. Cover the dish with a watch glass, and heat very gently with frequent stirring until decomposition is as complete as possible, adding a little nitric acid if undecomposed sulfides still remain. Finally, remove and rinse off the cover, evaporate to dryness, and finish in the usual way.

With chilled slag, the silica thus obtained is fairly pure. When there is much gelatinous silica, especial pains should be taken in the heating after evaporation so as to dehydrate it as thoroughly as possible. In technical work it usually suffices to heat the dry residue for half an hour or an hour, at a temperature of about 150°C .

II. SILICON OR TRUE SILICA

A. Application

The determination of silica is always called for in complete analyses, and its accurate valuation is often a time-consuming operation. In technical work it is not customary to follow all the requirements of exact analysis; the following procedure will give results accurate enough for most purposes.

B. Interfering Elements

Lead sulfate, silver chloride, barium sulfate, and tungstic acid are the most common interferences, and, when they are present in large amounts, separations are necessary. Special treatment must be given ores containing fluorine or boron. Columbium and tantalum will accompany silica and may cause an error by interfering with the complete volatilization of the silica by hydrofluoric acid. Potassium carbonate is to be avoided in fusions, when perchloric acid is used.

C. Procedure

With ores containing considerable matter soluble in acids, or constituents undesirable in the fusion, such as sulfides and compounds of reducible metals, it is usually best to give a preliminary treatment with acids and confine the fusion to the residue finally obtained, which may consist of mixed silica and undecomposed mat-

ter. Such ore is decomposed and treated, according to its nature, precisely as described for Insoluble Residue I, C, and the residue ignited in a platinum dish or crucible to burn off the filter paper. It need not be weighed.

a. Mix the ignited "insoluble residue," or 0.5 gram of the finely pulverized ore or silicate, if no preliminary treatment was given, in a platinum crucible or small platinum dish with about 5 grams of sodium carbonate and a small pinch of sodium nitrate to insure oxidation. Heat the mixture over a blast lamp, very slowly at first, so as to expel moisture without mechanical loss of substance. Raise the heat very gradually, so that much of the carbon dioxide may be driven off without causing any spattering, before the mass has actually fused to a liquid. Finally heat strongly to complete fusion of the mixture and continue the heating until bubbling has practically ceased and quiet fusion is attained. This may take from half an hour to an hour. If a crucible is used it is best to keep it covered to prevent loss from spattering. Pour the melt on a cold plate or on the crucible cover placed on a condenser as depicted in Chapter II, I, C, a.

b. Dissolve the melt adhering to the crucible and cover in a little dilute hydrochloric acid in a porcelain casserole, and, after removing and rinsing the crucible and cover, add the filtrate from the acid digestion to the dish, cover, and put in the poured melt. Add 5 ml. of nitric acid and more hydrochloric acid if necessary until the fusion is dissolved. Then evaporate to dryness at as high a temperature as possible to avoid spattering, and finish the drying on the water bath.

c. Wash down the sides of the dish with a fine stream of water and add 15 to 20 ml. of 70 per cent perchloric acid, or enough to insure a liquid mass at the fuming point. Heat the covered casserole until copious fumes are evolved and then for ten to fifteen minutes longer.

d. Cool slightly, add 75 ml. of water and 10 ml. of hydrochloric acid, heat to boiling, and filter off the impure silica on a rapid paper. Wash well with hot dilute hydrochloric acid (1 : 1) and finally with hot water. Draw off the excess moisture retained in the paper and residue with an aspirator, and place them in a weighed platinum crucible. Add 4 or 5 drops of dilute sulfuric acid, dry, and carefully

burn off the carbon, preventing the paper from bursting into open flame at any time. Finally, ignite at 1000°C . (Not above 850°C . when WO_3 is present), cool in a desiccator, and weigh as impure SiO_2 .

e. Cover the silica in the platinum crucible or dish with 2 or 3 ml. of water to prevent violent action, and then add 2 or 3 drops of strong sulfuric acid and 3 to 5 ml. of pure hydrofluoric acid. Evaporate the mixture to complete dryness. This is conveniently done on

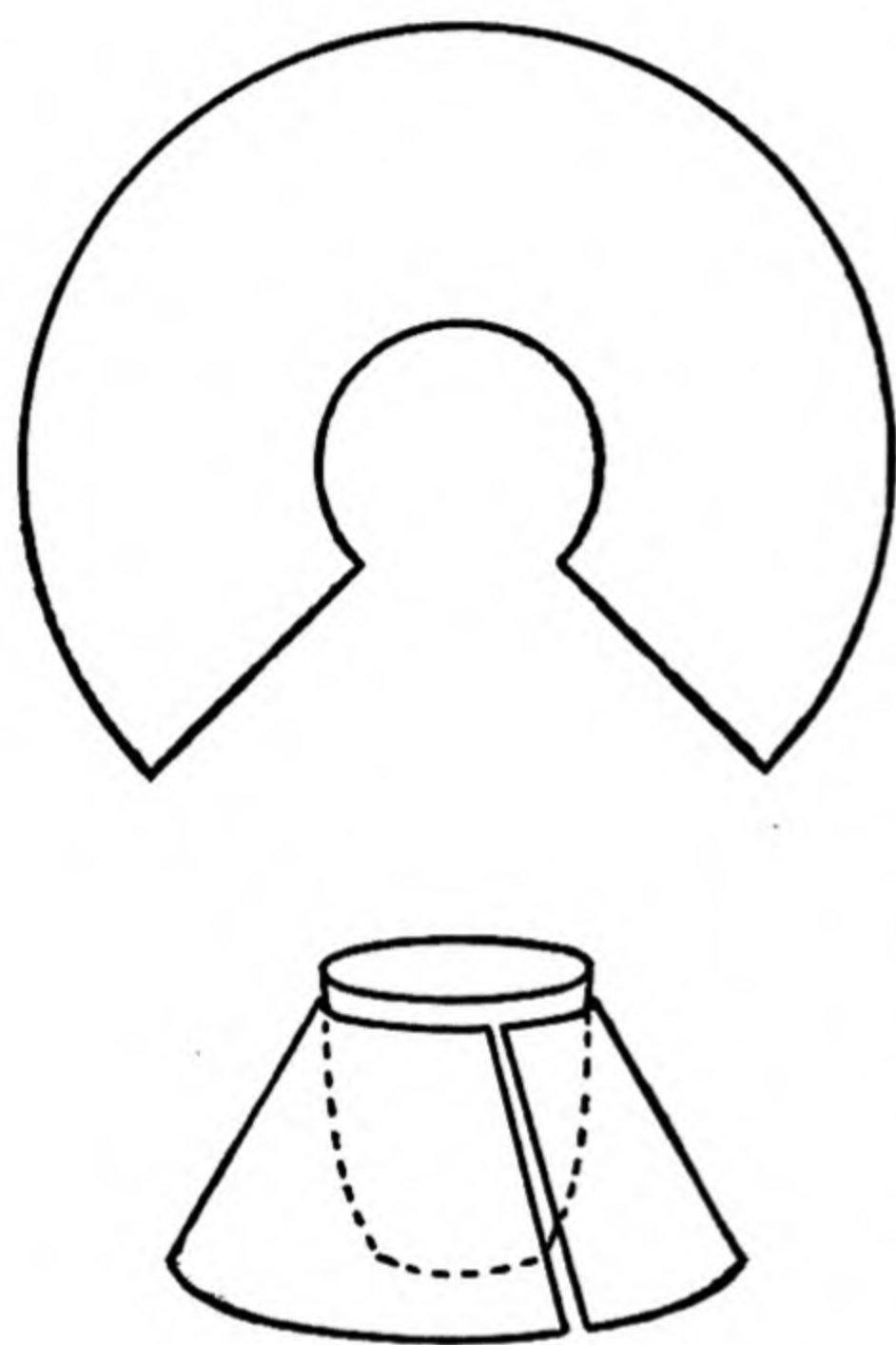


FIG. 16.

the hot plate, using an aluminum radiator as shown in Fig. 16. If there is a residue add a little more hydrofluoric acid and again evaporate. Repeat this procedure until no residue remains, or until there is no further diminution of the residue obtained. If the residue persists, add a drop or two of strong sulfuric acid, heat to dryness, ignite strongly over the blast lamp, cool, and weigh. Unless the amount of residue thus found is large, it will usually be sufficient to deduct its weight from that of the impure silica to obtain the true silica.

Barium sulfate in an ore would naturally contaminate the silica. Its amount could be determined and deducted as just described, or the weighed impure silica could be fused with alkali carbonate and the barium determined as sulfate.

D. Modifications

a. *Ores Containing Fluorine.* 1. Method of Schrenk and Ode. Dissolve the melt from the sodium carbonate fusion (which should be conducted at as low a temperature as possible) in 50 to 75 ml. of water and 15 ml. of 20 per cent perchloric acid saturated with boric acid at 50°C . Evaporate to a small volume, add 15 ml. of strong perchloric acid, and take to fumes for about five minutes. Wash down the sides with a few milliliters of water and repeat the fuming for five minutes longer. Continue as in C, d, and e.

2. Method of Hoffman and Lundell.² Fuse 0.5 gram of the sample (dried at 105° C.) with 5 grams of sodium or potassium carbonate, leach the cooled melt with hot water, and filter when disintegration is complete. Return the insoluble residue to the dish by a jet of water, add 50 ml. of a 2 per cent solution of sodium carbonate, boil for a few minutes, filter, and wash thoroughly with hot water. Reserve the residue (1). To the combined filtrates, in a volume of about 300 ml., add 1 gram of zinc oxide dissolved in 20 ml. of nitric acid (1 : 9), boil for one minute, filter, and wash with hot water. Reserve the precipitate (2). Add a few drops of methyl red indicator to the filtrate, nearly neutralize with nitric acid, and evaporate to 200 ml., taking care that the solution remains alkaline during evaporation. Finish the neutralization by adding nitric acid (1 : 9) until the color is a very faint pink. Now add 1 gram of zinc oxide dissolved in ammonium hydroxide and ammonium carbonate,³ and boil in a covered platinum dish until the odor of ammonia is entirely gone. This usually requires boiling to a volume of about 50 ml. Add 50 ml. of warm water, stir, allow to stand for a few minutes, filter, and wash the precipitate (3) with cold water.

Transfer the insoluble residue (1) and the precipitates (2) and (3) from the papers to the platinum dish by means of a jet of hydrochloric acid (5 : 95). Ignite all the papers, and add the ash to the dish. Now add 25 ml. of hydrochloric acid, and evaporate to dryness on the steam bath. Drench the residue with 10 ml. of hydrochloric acid and 100 to 150 ml. of water. Heat, filter, and wash with hot hydrochloric acid (5 : 95) and then with hot water. Return the filtrate and washings to the platinum dish, add 10 ml. of sulfuric acid, and evaporate to fumes. Cool, add 100 to 150 ml. of warm water, digest until salts are in solution, filter, and wash with hot water.

Place the two papers containing the silica in a weighed platinum crucible, dry, char the paper without inflaming, burn off the carbon, and finally ignite at 1200° C. Cool in a desiccator, weigh, and re-heat until a constant weight is obtained. Proceed as in C, e.

² J. I. Hoffman and G. E. F. Lundell, *Bur. Standards J. Research*, **3**, 581, 1929, by permission of Dr. Lundell.

³ Transfer 1 gram of zinc oxide and 2 grams of ammonium carbonate to a small beaker, add 20 ml. of water and 2 ml. of ammonium hydroxide, and digest on the steam bath until a clear solution is obtained.

b. *Ores Containing Boron.* Evaporate the residue from the first dehydration (C, b) to dryness, twice, with 20- to 30-ml. portions of methyl alcohol saturated with hydrochloric acid gas. Proceed as in C, d. The boron is volatilized as methyl borate, $B(OCH_3)_3$.

c. *Peroxide Fusion Method for Silica.* This method is very convenient and frequently serves admirably where other methods, even the carbonate fusion, are unsatisfactory.

Treat 0.5 gram of the finely ground material exactly as described in Molybdenum, II, C, a, up to the point where the crucible has been removed from the melt disintegrated in water. Now transfer the mixture to an evaporating dish of sufficient size, cover the dish, and add hydrochloric acid in excess, cautiously, to avoid loss by effervescence. Continue and finish as described in C, b, c, d, and e.

If iron or nickel is to be determined in the same portion as the silica, a nickel crucible may be used for iron and an iron one for nickel. When an iron crucible is employed see that any scales of iron oxide from the crucible are entirely dissolved, before completing the evaporation to dryness, adding more acid if necessary.

Metallurgical products containing carbon, which may be particularly difficult to decompose completely by a carbonate fusion, yield readily to the peroxide fusion; in fact, the method is almost always applicable where a fusion is necessary. Always heat slowly to avoid loss by spattering, or by scintillation due to sulfides or organic matter.

SULFUR MINERALS

Mineral Name	Chemical Formula	% S	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Native sulfur	S	90-99.9	White to yellow	2.1	Ca, Si, Se, C, As	Soluble in CS ₂ or aniline	Na ₂ O ₂ , Na ₂ CO ₃ +KNO ₃
Pyrite	FeS ₂	53.4	Black, metallic luster	5.0	Si, Cu, Pb, Zn, Ca, Mg, Ba, As, Ni, Co, Tl	HNO ₃ + oxidizing agent	Na ₂ CO ₃ + oxidizing agent
Pyrrhotite	Fe _n S _{n+1}	Variable	Black, metallic luster	4.6	Same	Same	Same
Marcasite	FeS ₂	53.4	Greenish black, metallic luster	4.9	Same	Same	Same

Sulfur is found combined with antimony, arsenic, bismuth, cadmium, cobalt, copper, iron, lead, mercury, molybdenum, nickel, selenium, silver, tellurium, tin, and zinc, to form important sulfide ore minerals. Sulfides of chromium, germanium, manganese, platinum, thallium, tungsten, and vanadium are of infrequent occurrence. Barium, calcium, copper, lead, magnesium, and strontium, in combination with sulfur as sulfates, are ores of these elements; sulfates of aluminum, potassium, and sodium, are of commercial importance; and sulfates of cobalt, iron, lithium, manganese, nickel, uranium, vanadium, and zinc are occasionally found in nature.

CHAPTER XXV

SULFUR

I. FUSION METHOD¹

A. Application

The following procedure is adaptable to nearly all types and grades of ores. For oxidized ores or materials low in sulfides, fusion with sodium carbonate and potassium or sodium nitrate (Fresenius) is preferable. Other fusion methods to be found in the literature are those of (1) Eschka, using sodium carbonate and magnesium oxide; (2) Ebaugh and Sprague, using sodium carbonate and zinc oxide; and (3) Böckmann, using sodium carbonate and potassium chlorate.

B. Interfering Elements

Elements which hydrolyze or precipitate in weak hydrochloric acid solution, such as lead, antimony, bismuth, titanium and zirconium, may cause difficulties. The reducible elements such as the first three mentioned above may be easily removed by metallic aluminum, zinc, or magnesium. Excessive amounts of salts of ammonia, the alkalis, alkaline earths, and a number of the members of the ammonium sulfide group tend to coprecipitate with and contaminate the barium sulfate precipitate.

C. Procedure

a. Weigh 0.5 gram of finely ground substance. Mix in a small spun-iron crucible (about 25- to 30-ml. capacity) with 1 gram of dry sodium carbonate and about 5 grams of sodium peroxide. Use peroxide of calorimeter quality, and, after trial, it may be measured instead of weighed. Place the crucible in a hole cut in asbestos board, to prevent absorption of sulfur fumes, and fuse at a gentle heat over a Bunsen burner. Heavy sulfides may require the admix-

¹ J. Clark, *J. Chem. Soc.*, 63, 1079, 1893.

ture of more sodium carbonate to prevent deflagration and possible loss.

Set the crucible, while still quite hot, in about $\frac{1}{2}$ inch of cold water contained in a 400-ml. beaker. Cover the beaker and upset the crucible with a glass rod. The contents will quickly disintegrate. Remove and wash the crucible. Add about 5 grams of ammonium carbonate to destroy partly the causticity of the peroxide, warm gently until dissolved, and then filter through an 11-cm. filter. A small wad of absorbent cotton, placed in the point of the filter and wetted, will facilitate the filtration. A Witt's plate and suction is a better combination for filtering, and renders unnecessary the use of ammonium carbonate. Wash at least ten times with hot water. Receive the filtrate in a 400-ml. beaker, or transfer to it subsequently. If the filtrate is greenish, indicating manganese, it is a good plan to add 5 ml. of alcohol, boil, and then filter again.

b. Add a drop or two of methyl orange as indicator, make just acid with hydrochloric acid, and then add 1.2 ml. of the strong acid in excess. Now dilute to 300 ml. with hot water, having previously placed a mark on the beaker at this point.

c. Heat the solution to boiling and add 10-15 ml. of a 10 per cent solution of barium chloride. This is best done through a small funnel supported over the beaker, and having the stem drawn out to a very small opening, so that it will take several minutes to deliver the barium chloride. Now cover the beaker and set aside to settle for an hour or two. This will suffice for ordinary technical work, but in exact analyses the beaker should always be allowed to stand overnight. Filter through a double ashless filter. Unless the filtrate appears perfectly clear, run it through a second time. Wash ten times with hot water. Test the filtrate with a little more barium chloride to be sure that precipitation is complete. Transfer the moist filter and precipitate to a weighed porcelain or platinum crucible. Wipe out any precipitate adhering in the funnel with a piece of dry filter paper, and add to the rest. Ignite by first heating very gently until dry, and then at dull redness until the residue is perfectly white. A high temperature, such as that of a blast lamp, is neither necessary nor desirable. Cool in a desiccator and weigh, deducting the weight of the filter ash, or the blank if one has been run.

Multiply the weight of the barium sulfate by 0.1373 to obtain the weight of the sulfur.

d. It is best to run a blank, once for all, with all the reagents employed, and always deduct for any sulfur thus found. The treatment of the blank should include the fusion in the iron crucible.

In filtering the barium sulfate precipitate, observe the following precaution: after the precipitate has apparently all been transferred to the filter, do not fail to rub the inside of the beaker thoroughly with a "policeman" and a little water, even though the beaker appears perfectly clean. An appreciable amount of sulfate can usually be found.

Ordinarily it is unnecessary to test the filtrate from the barium sulfate with more barium chloride, unless the precipitate is large in amount, or the percentage of sulfur found approximates the total quantity that the barium chloride used is capable of precipitating.

Ten milliliters of a 10 per cent solution of barium chloride is the equivalent of 0.1312 gram of sulfur, or, on the basis of 0.5 gram of ore taken, 26.24 per cent. Of course a moderate excess is necessary in order to effect as complete a precipitation as possible. With high percentages of sulfur it is better to start with less ore than to use a large amount of barium chloride.

When barium sulfate is precipitated, it tends to occlude other salts in solution, especially ferric iron. This tendency is increased by an excess of hydrochloric acid. Barium sulfate is also appreciably soluble in hydrochloric acid. Hydrochloric acid must be present, however, and the best results appear to be obtained with an excess of 0.3 ml. per 100 ml. of solution. Ferrous iron causes less contamination than ferric, and, though advantage may be taken of this fact, it is usually best to remove iron entirely before precipitation.

Too high a temperature, such as the blast lamp, during the ignition of barium sulfate, may cause a gradual decomposition and loss of sulfur trioxide. A temperature of dull redness is all that is necessary for the ignition.

Another possible source of error is a partial reduction of the sulfate to sulfide by the burning filter paper. Continued heating with free access of air usually corrects this. Both these errors may be corrected, after cooling, by adding a drop of sulfuric acid and again

igniting carefully. Certain errors due to occluded salts cannot be corrected, and it is therefore best to avoid them, as far as possible, by proper conditions of precipitation.

II. DECOMPOSITION BY WET OXIDATION

A. Application

This method, though not applicable to insoluble sulfates such as barium and strontium sulfates, serves as a rapid routine procedure when the highest accuracy is not necessary. When greater accuracy is desired the decomposition method of Allen and Bishop² with liquid bromine, carbon tetrachloride, and nitric acid is recommended. Other wet oxidation methods are those of Lunge, using aqua regia, and of Smoot, using nitric and hydrochloric acids with liquid bromine.

B. Interfering Elements

The interferences, in addition to those described in the preceding method, are the possibility of losses due to incomplete decomposition or to volatilization of part of the sulfur.

C. Procedure

a. Treat an appropriate weight of the ore in a 250-ml. beaker with 10 to 25 ml. of nitric acid saturated with potassium chlorate. The weighed material should be spread evenly over the bottom of the beaker and wet with water according to the amount of free sulfide or sulfur in the sample. Heat gently until the red fumes have somewhat abated, then on a warmer portion of the plate. The acid should not be boiled violently, as this would unnecessarily weaken it. On the other hand, it is best not to allow it simply to simmer, as the explosive gases from the decomposing chlorate may then collect in the beaker and produce annoying, although not dangerous, explosions. When the sulfur has entirely disappeared the solution should be boiled to complete dryness. After cooling, add 5 ml. of strong hydrochloric acid. This should be done cautiously to avoid a too violent reaction with the undecomposed potassium chlorate that may be present. If iron oxide, etc., still remains undissolved, gently heat the hydrochloric acid mixture until solution is as com-

² W. S. Allen and H. B. Bishop, *J. Ind. Eng. Chem.*, 11, 46, 1919.

plete as possible, adding more acid if necessary. Finally, boil to dryness; then add 5 ml. more of the hydrochloric acid and again boil to dryness. This is to decompose nitrates and expel all nitric acid. Take up once more in 5 ml. of hydrochloric acid and dilute with about 100 ml. of cold water. Make alkaline with ammonia, and then add 10 ml. of a saturated solution of ammonium carbonate. This is to convert any lead sulfate to carbonate and thus render the combined SO_3 soluble, as ammonium sulfate. Heat to boiling, allow the ferric hydroxide, etc., to settle, and then filter and wash very thoroughly with hot water, receiving the filtrate in a 400-ml. beaker. Proceed with the filtrate as described in I, C, b.

TIN MINERALS

Mineral Name	Chemical Formula	% Sn	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Cassiterite.....	SnO ₂	78.6	White to yellowish or brownish	7.0	Fe, Mn, W, Ta, Mo, Si, As, Bi, Zn, Au, Pb, Zr, B, F		NaOH, KOH, Na ₂ O ₂
Stannite.....	Cu ₂ S·FeS·SnS ₂	27.5	Black to greenish black, metallic luster	4.4	Ag, Sb, Mn, B, F, As, Au, Pb	HNO ₃ (partly)	Na ₂ O ₂

Tin is found in a few rare sulfide minerals in combination with silver, lead, antimony, and germanium; also in the silicates, stokesite and arandisite; and the borates, hulsite and nordenskioldine. Tin has been found native in a few localities.

The chief difficulties encountered in tin analyses are from losses due to incomplete decomposition, hydrolysis, and the volatility of stannic chloride. Ores containing cassiterite are often extremely difficult to decompose, even on protracted fusion.

CHAPTER XXVI

TIN

I. PEARCE-LOW METHOD

A. Application

This method is applicable to nearly all grades and types of tin ores and gives excellent results when certain conditions are closely observed. Various modifications have been proposed, both in the method of decomposition and the type of reducing agent. The following procedure has given good results on refractory tin ore from Bolivia.

B. Interfering Elements

Copper, in appreciable amounts, is the most common interference. Elements partly or wholly reduced by nickel in strong acid solution and then oxidized by the iodine solution will give high results. Of these, molybdenum and vanadium may be occasionally encountered. Oxidizing agents such as nitric acid and ferric chloride (derived from iron scale from the crucible) will cause low results; and excessive amounts of elements which produce colored solutions, such as tungsten or nickel, may mask the end point.

C. Procedure

a. Grind a portion of the sample in an agate mortar to an impalpable powder, and weigh out an amount from 0.2 to 1.0 gram according to the grade of the material.

Melt about 8 grams of pure potassium hydroxide pellets in a 50- or 60-ml. nickel crucible until the moisture is expelled and quiet fusion attained. Allow to cool, and spread the weighed powdered sample over the top of the cake. Sprinkle enough sodium peroxide over the top to oxidize the estimated amount of sulfides present. In dealing with oxidized material the sodium peroxide should be omitted and a little powdered charcoal added to the potassium hydroxide before melting. Cover the crucible and set in a hole made in an

asbestos shield so that the crucible is about one-quarter of an inch from the top to the asbestos. Heat extremely cautiously until any violent reaction with the peroxide has subsided, then at a low temperature, guarding carefully against boiling over, until spattering has stopped and finally for one-half hour with the full flame of the Bunsen burner until the fusion is quiescent. Remove and reserve the cover, and pour the melt upon a clean iron plate. Invert an evaporating dish over the hot cake, to prevent loss should the cake crack apart violently on cooling.

b. Set the empty crucible in a 250-ml. beaker containing 50 ml. of cold water. Cover the beaker and tip the crucible over with a glass rod, so as to admit the water; then add 10 ml. of strong hydrochloric acid. Warm the mixture, and turn the crucible about with the glass rod until it appears clean. Remove and rinse the beaker cover, lift the crucible on the rod, and wash off the outside, so as to permit handling with the fingers. Now rinse out the inside of the crucible. If any undissolved melt remains, dissolve it with a little hydrochloric acid and rinse into the beaker. Treat the crucible cover in the same manner. Again cover the beaker and add the cooled melt. Warm until the cake has dissolved.

c. Transfer the solution and any residue to a 500-ml. Erlenmeyer flask (marked for a volume of 200 ml.), and wash the beaker carefully. Make the solution in the flask acid with hydrochloric acid and add just 50 ml. of concentrated acid in excess; then dilute to the 200-ml. mark. Swirl the contents of the flask so as to bring any residue into a small heap in the center of the bottom of the flask, and examine carefully for undecomposed material. Any light-colored grains present will show incomplete decomposition of the cassiterite, and the fusion had best be repeated, giving more time to effect the decomposition. Ignore any black scales from the nickel crucible, or free carbon particles if charcoal was used.

Add a strip of sheet nickel, 1 inch by 5 to 7 inches in length, rolled into a scroll, cover the flask with a porcelain crucible or small watch glass, and heat to boiling. Move to a cooler portion of the plate and allow to boil gently until the iron is reduced then for 40 to 60 minutes longer. The solution should be a clear, light green color. If blue, brown, or purplish, the presence of tungsten, molybdenum, or vanadium is denoted.

d. Remove from the hot plate, quickly add a pinch of sodium or calcium carbonate, and stopper tightly with a one-hole rubber stopper plugged with a glass rod, then cool immediately under the faucet or preferably in ice water. When thoroughly cold, remove the glass plug from the stopper and quickly introduce about 5 ml. of starch solution by means of a pipet.

Insert the tip of a 25-ml. buret filled with a standard iodine solution, through the hole, well into the flask, and titrate to a faint, permanent blue tinge. Rotate the flask gently after each addition of iodine, and do not withdraw the buret tip during the titration.

Multiply the number of milliliters of iodine solution used by the percentage value of 1 ml. to obtain the percentage of tin.

For the preparation and standardization of the iodine solution, see **Chapter XXXIII**.

D. Modifications

a. Pure iron may be used in place of nickel for the reduction; it seems to accomplish that purpose in less time. The iron, however, must be removed from the solution before titrating, but the nickel may be left in the solution. A convenient form of hanger, made from glass rod, and holding about a dozen bent pure-iron horse-shoe nails, is shown in **Fig. 17**. Hillebrand and Lundell¹ recommend the use of test lead for the reduction of the tin.

b. Rupp² has recently introduced a modification of this method by titrating with chloramine-T in place of iodine. After reducing and cooling, the acidity is lowered by sodium hydroxide containing sodium carbonate, a crystal of potassium iodide and starch solution added, and the liquid then titrated with 0.10 *N* chloramine-T to the usual blue end point. 1 milliliter = 5.935 mg. of tin. The reagent has the advantage that it is more stable than iodine solution.

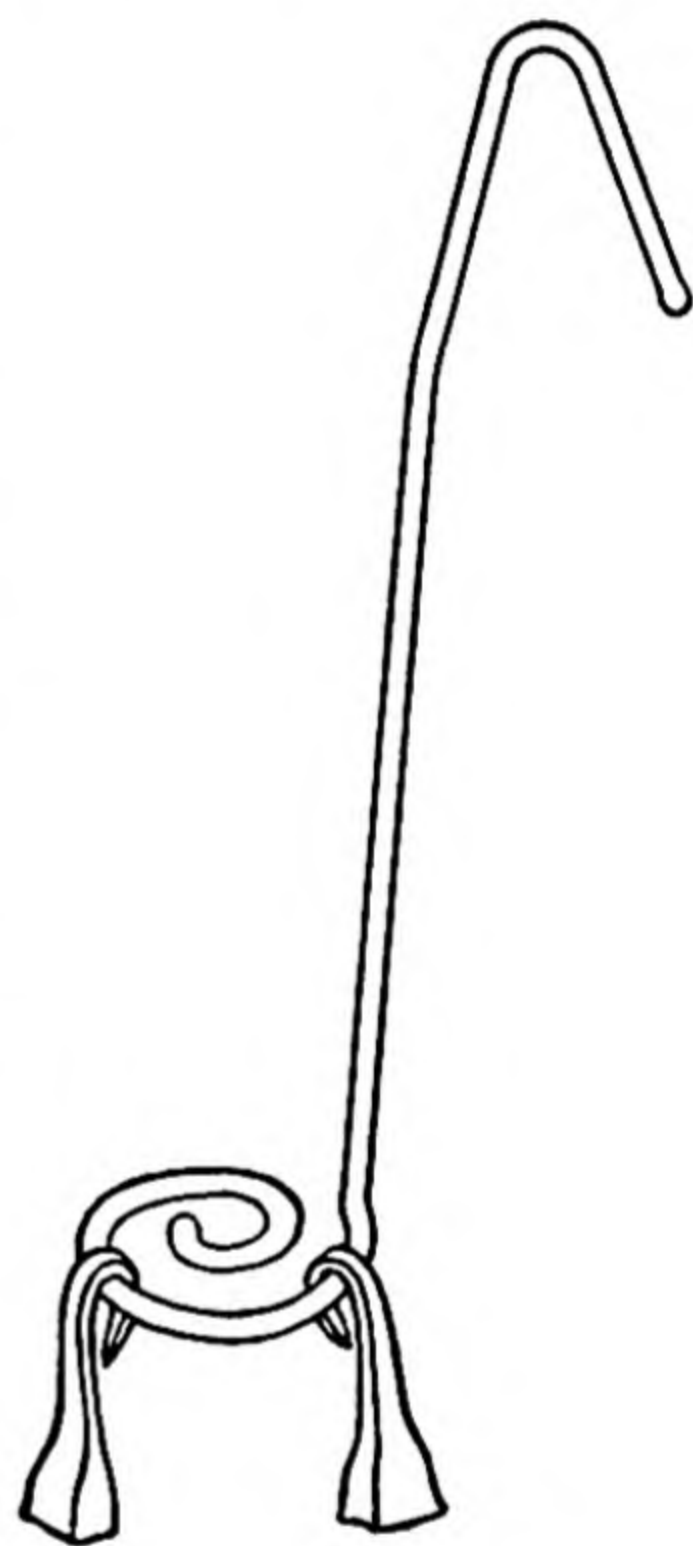


FIG. 17.

¹ Applied Inorganic Analysis, p. 239, John Wiley & Sons, Inc., 1929.

² Rupp, *Z. anal. Chem.*, 73, 51, 1928.

c. *Procedure for Ores Containing Large Amounts of Copper.* Place the pulverized and weighed sample in a platinum dish and digest to a small volume with 10 ml. of nitric and 10 ml. of hydrofluoric acids. Add 2 or 3 ml. of concentrated sulfuric acid and take to dryness, then heat gently over the gas flame until the fumes of SO_3 are expelled.

The cooled mass is taken up with a little water and the whole transferred to a 150-ml. beaker, scrubbing the platinum dish well with a policeman. Add 15 ml. of hydrochloric acid (1 : 1), cover, and warm gently till all soluble salts are in solution. Add 0.5 gram of iron (by hydrogen), and allow the reaction to continue until the iron is entirely consumed. Practically all the copper is reduced to the metal and will carry down about 2 per cent of the soluble tin. The copper left in solution is not enough to interfere in the subsequent reduction and titration. Filter off the copper-tin precipitate and insoluble (such as cassiterite), receiving the filtrate in a 400-ml. beaker.

Wash the precipitated metals and insoluble carefully off the filter paper into a 400-ml. beaker, and reserve the paper. The precipitated copper and tin are dissolved in a few milliliters of nitric acid, diluted to 300 ml. with boiling water, and allowed to stand on the steam plate (preferably overnight) until the metastannic acid is settled and the solution is clear. The metastannic acid along with the insoluble is then filtered off on a close paper and washed with hot water. The two filter papers and contents are carefully ignited in a nickel crucible and fused with potassium hydroxide as described in C, a, the melt being dissolved in the original filtrate in the beaker. Proceed as in C, c, and d.

TITANIUM MINERALS

Mineral Name	Chemical Formula	% TiO ₂	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Rutile.....	TiO ₂	90-100	White to gray or pale brown	4.1	Fe, Zr, Cb, Ta, Si, Al, Mn, Ca, Mg, Ba, Na, K	H ₂ SO ₄ +HF (difficultly)	KHSO ₄
Octahedrite...							
Brookite.....							
Ilmenite.....	FeO·TiO ₂	52.7	Reddish-brown to black	4.5	Same	HCl (difficultly)	KHSO ₄
Titanite.....	CaO·TiO ₂ ·SiO ₂	40.8	White or tinted	3.5	Fe, Mn, Mg, Zr, F, Na, K	H ₂ SO ₄ +HF	Na ₂ CO ₃

Titanium is a common constituent of iron and aluminum ores, and is found in small amounts in a great many minerals and rocks, usually in combination with iron, manganese, zirconium, aluminum, calcium, magnesium, silica, columbium, tantalum, thorium, or the rare earths. It is frequently encountered in gangue minerals such as pyroxenes, amphiboles, chlorites, garnets, and micas.

Titanium ores, relatively free from silica, are most easily decomposed by an acid flux followed by solution of the melt in an acid medium of high enough strength to prevent hydrolysis. Titanium causes trouble in analytical work by the ease with which its salts hydrolyze, and is often a source of error in analyses for elements such as silica, iron, aluminum, and beryllium.

CHAPTER XXVII

TITANIUM

I. CUPFERRON METHOD¹

A. Application

Cupferron, the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N \cdot NO \cdot ONH_4$, precipitates titanium, as a voluminous canary yellow precipitate, from mineral acid solution. The method is applicable to all classes of material containing from moderate to small amounts of titanium, the bulk of precipitate causing difficulties in the analysis of high-grade titanium ores.

B. Interfering Elements

Columbium, tantalum, and zirconium are precipitated quantitatively with the titanium. In the absence of appreciable amounts of silica, tungsten, phosphorus, and vanadium, the method may be shortened considerably.

C. Procedure

a. Fuse 0.5 gram (or smaller amount for higher contents of titanium) of the ore in a platinum crucible with 5 to 6 grams of sodium carbonate and a little sodium nitrate until the melt is clear. Pour the melt on a cold plate, and dissolve it and the part adhering to the crucible and cover in a minimum amount of water in a porcelain or nickel dish. Add 10 grams of sodium hydroxide² pellets, and heat to boiling. Allow to cool, and filter on a strong paper. Discard the filtrate. Wash the precipitate back to the dish, and, after covering, dissolve the carbonates with a little hydrochloric acid and dilute to about 75 ml. Boil off the carbon dioxide and precipitate the titanium with the hydroxides of the ammonia group by the addition of an excess of ammonium hydroxide. Heat to

¹ O. Baudisch, *Chem. Ztg.*, **33**, 1298, 1909; W. M. Thornton, *Chem. News*, **110**, 5, 1914; G. E. F. Lundell and H. B. Knowles, *Ind. Eng. Chem.*, **12**, 344, 1920.

² W. R. Schoeller, *The Analytical Chemistry of Tantalum and Niobium*, Chapman & Hall, Ltd., London, pp. 91 and 92.

boiling, and filter on the same paper as before. Wash with a hot 2 per cent solution of ammonium nitrate and proceed as in b. When only small amounts of silica are present and tungsten and vanadium are known to be absent (as determined by preliminary spot tests) the preceding manipulation may be omitted and the original material fused with bisulfate as follows in b.

b. Dry and ignite the ammonia precipitate obtained in a in a silica crucible, and fuse with potassium bisulfate. The amount of flux necessary should be judged by the volume of residue or material to be fused. Dissolve the melt in a 100 ml. of water containing 5 ml. of sulfuric acid and 10 grams of tartaric acid, in a 250-ml. beaker. Warm until all is dissolved (a little silica may remain as a residue), and remove the crucible and cover and rinse with a little water.

c. Pass hydrogen sulfide gas into the solution until all the iron is reduced. If a precipitate is formed, filter it off. If no members of the acid sulfide group are present make the solution alkaline with ammonium hydroxide and allow the precipitate of iron sulfide to coagulate and settle. Filter and wash with a dilute solution of ammonium sulfide containing a little ammonium tartrate.

d. Boil the filtrate in a 400-ml. beaker for about 10 minutes. Remove from the plate and acidify the solution with sulfuric acid (1 : 1) and add 40 ml. in excess. Continue the boiling until a lead acetate test paper held over the beaker no longer gives a test for H_2S . Remove from the plate, allow to cool slightly, and oxidize with potassium permanganate³ solution. Dilute to 200 ml. and cool with crushed ice or in a refrigerator. Precipitate the titanium with an excess of a 6 per cent water solution of cupferron while stirring, let set for about ten minutes with occasional stirring, and filter on a rapid ashless paper. A little paper pulp stirred in will aid filtration. Wash the precipitate well with ice water containing about 1 per cent of sulfuric acid and 0.5 per cent of the reagent.

e. Draw off the excess moisture from the precipitate and paper by suction, and place the folded paper and contents in a porcelain crucible. Dry slowly on the hot plate and char, then ignite to TiO_2 , cool, and weigh.

³ Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 110, John Wiley & Sons, Inc., 1929.

f. The precipitate of titanium with cupferron should be bright yellow in color. If brownish, iron has not been completely separated; if light in color, the earth acids or zirconium are probably present in quantity. Fuse the ignited TiO_2 in a silica crucible with potassium bisulfate and proceed by Schoeller's⁴ method of separation as follows:

Extract the melt with a 1 per cent tannic acid solution in 5 per cent sulfuric acid (1 gram of tannic acid dissolved in 90 ml. of water and 10 ml. of sulfuric acid, 1 : 1). Heat to boiling until the melt is well broken up, and set aside till cold. Filter off the insoluble tantalum and columbium complexes and wash with 5 per cent sulfuric acid. Add 10 ml. of sulfuric acid to the filtrate, and boil down until it darkens and foams. Burn off the carbon with repeated additions of nitric acid, and finally take to strong fumes. Cool; add 100 ml. of cold water and an excess of hydrogen peroxide. Add 1 gram of ammonium phosphate⁵ and allow to stand warm for two hours. Filter off the zirconium phosphate, dry and ignite to $\text{Zr}_2\text{P}_2\text{O}_7$ containing 46.3 per cent ZrO_2 . Ignite the earth acid complexes to the oxides and obtain the TiO_2 by difference.

II. METHOD OF GOOCH⁶

A. Application

This method is applicable to minerals and metallurgical products that are comparatively high in titanium. The method provides for the separation of titanium from iron, aluminum, and phosphoric acid, with which it commonly occurs. The procedure, as proposed by F. A. Gooch and modified for non-aluminous rocks by Wm. M. Thornton, has been found by Scott to give reliable results. The details of the method, with a few slight changes found to be advantageous, are given below. Iron is separated from titanium by precipitation as the sulfide in the presence of tartaric acid; the organic acid is destroyed by oxidation and the titanium precipitated from a boiling acetic acid solution. In the presence of alumina and

⁴ W. R. Schoeller, *The Analytical Chemistry of Tantalum and Niobium*, p. 118, Chapman & Hall, Ltd., London, 1937.

⁵ W. F. Hillebrand, *The Analysis of Silicate and Carbonate Rocks*, *U. S. Geol. Survey Bull.* 700, 1919, p. 174.

⁶ F. A. Gooch, *Proc. Am. Acad. Arts Sci.*, 12, 435, 1885.

phosphoric acid the impure precipitate is fused with sodium carbonate and the impurities leached out.

B. Interfering Elements

This method fails in the presence of zirconium.⁷ Aluminum, iron, tungsten, silica, vanadium, and elements that hydrolyze in acetic acid solution must be removed.

C. Procedure

a. Proceed as in I, C, a, or b and dissolve the melt in 100 ml. of 10 per cent sulfuric acid containing 1 gram of tartaric acid. The melt should not contain more than about 0.2 gram of titanium, as this would require more tartaric acid to hold it in solution and would be troublesome in the subsequent removal of the organic acid. Continue as in I, C, c.

b. The tartaric acid must be removed, since titanium cannot be precipitated in its presence. Transfer the filtrate to a 500-ml. Kjeldahl flask, add 15-20 ml. of strong sulfuric acid, and boil until incipient charring occurs. Cool slightly, add about 10 ml. of fuming nitric acid, very cautiously, a few drops at a time, and when the first violent action has subsided heat the flask gradually (under a hood). A vigorous reaction will take place, accompanied by much effervescence and foaming, with evolution of copious brown fumes. The organic matter will gradually disappear, the effervescence becoming steady and finally ceasing, and white fumes of SO_3 will appear. Cool the solution and pour the pale yellow syrup into 100 ml. of cold water. Wash out the flask, adding to the rest. Filter the solution if it is cloudy.

Add ammonia until the solution is nearly neutral. This point may be recognized by the production of a slight turbidity, which clears by vigorous stirring. If a trace of iron is suspected, add about 1 ml. of a 10 per cent solution of ammonium acid sulfite. Now add 5 ml. of glacial acetic acid, then 15 grams of ammonium acetate, and make up the volume of the solution to about 350 ml. Heat rapidly to boiling and maintain in ebullition for about three minutes. The titanium will precipitate in a white, flocculent, and readily filterable condition. Filter off the precipitate, washing first with

⁷ W. F. Hillebrand, *U. S. Geol. Survey Bull.* 700, p. 162.

water containing acetic acid and finally with pure water. Ignite filter and precipitate, at first cautiously over a low flame, and then intensely for twenty minutes. Weigh the residue as TiO_2 .

III. COLORIMETRIC METHOD⁸

A. Application

This method is the most rapid and convenient for the average analysis of titanium in materials such as limestone, clays, and iron ores when the amount of titanium present does not exceed a few milligrams and is conveniently collected in the ammonia precipitate during the course of an analysis for silica, alumina, etc.

B. Interfering Elements

Elements forming colored sulfuric acid solutions, the most common of which are chromium, cobalt, iron, and nickel, and rarely selenium, tellurium, or members of the platinum group, interfere when present in quantity. Small amounts present in the materials may be handled if a like amount is added to the comparison standard before the addition of the hydrogen peroxide. Vanadium, molybdenum, and cerium react with hydrogen peroxide to give colored solutions which may be mistaken for and counted as titanium. Certain other elements interfere by their bleaching action on the colored titanium compound. These are fluorine, phosphorus, the alkalis (in excessive amounts), and arsenic,⁹ and they must be removed before the comparison is made.

C. Procedure

Fuse 0.5 gram of the material (or the dried and ignited ammonia precipitate from an ordinary analysis) with potassium bisulfate in a silica crucible. Take up the melt in 10 per cent sulfuric acid, and filter off any insoluble material. To the solution or an aliquot part add 1 ml. of hydrogen peroxide and compare the color (orange-red to yellow) with that of solutions containing known amounts of titanium, and the same amounts of sulfuric acid and hydrogen peroxide as the unknown. Nessler tubes may be used

⁸ A. Weller, *Ber.*, 15, 2593, 1882.

⁹ Lundell and Hoffman, *Outlines of Methods of Chemical Analysis*, p. 171, John Wiley & Sons, Inc., 1938.

for this purpose, and the solutions are all brought to the same volume with 10 per cent sulfuric acid. See **Chapter XXXIII** for the preparation of the standard titanium solution.

The colors produced are more or less affected by the presence of iron, and it is therefore advisable to add to the comparison tubes an amount of ferric sulfate corresponding approximately to that in the solution which is being tested. A solution of ferric ammonium alum answers well for this purpose, and all that is necessary is to match the color of the solution of the mineral before adding hydrogen peroxide to it. If this is done, titanium can be readily determined in the presence of very considerable amounts of iron. Thus, 0.02 mg. of titanic oxide can be detected in 30 ml. of water in the presence of 0.1 gram of ferric oxide in the form of sulfate. This would correspond to 0.02 per cent for 0.1 gram of mineral.

The color produced by titanium is destroyed by hydrofluoric acid or fluorides. Vanadium produces a very similar color, which, however, is not thus destroyed. A method of distinguishing between the two elements as a qualitative test is as follows: Divide the solution in two test tubes. Add to one 5 ml. of water and to the other 5 ml. of 3 per cent hydrogen peroxide solution. If titanium alone is present the peroxide tube will show a yellow or orange-yellow tinge when compared with the other. A distinctly reddish tinge indicates vanadium, with titanium also possibly present. Add 0.05 *N* ferrous sulfate solution, 1 ml. at a time, shaking after each addition. The red color will gradually fade. If it fades to a yellow, titanium is present; otherwise it will fade out without changing to yellow.

TUNGSTEN MINERALS

Mineral Name	Chemical Formula	% WO ₃	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Ferberite.....	FeWO ₄	76.7					
Wolframite.....	(FeMn)WO ₄	Variable	Dark brown to black	7.0	Sn, Bi, Pb, Zn, Ca, Mg, S, Si, F, Mo, Cu	Aqua regia (leaving WO ₃)	Na ₂ CO ₃
Hübnerite.....	MnWO ₄	76.8					
Scheelite.....	CaWO ₄	80.6	White or tinted	6.0	Same as above	HCl, HNO ₃ (leaving WO ₃)	Na ₂ CO ₃
Tungstic ocher.....	WO ₃ ·Fe ₂ O ₃ ·6H ₂ O	36.0	Pale yellow to brownish		Same as above	HCl, HNO ₃ (leaving WO ₃)	Na ₂ CO ₃

Tungsten occurs as the sulfide in tungstenite, as the hydrous oxide in tungstite, with lead in stolzite and raspite, with molybdenum in powellite and chillagite, and with copper in cuprotungstite and cuproscheelite.

Most tungsten ores will yield to acid treatment, leaving the main part of the tungsten as WO₃ with the "insoluble." For complete solution, alkaline fusions must be resorted to.

CHAPTER XXVIII

TUNGSTEN

I. LOW'S METHOD

A. Application

Tungsten in ores is usually reported as the oxide, WO_3 , instead of the element. Most of the methods described for its determination are very tedious, either in the original decomposition of the ore or in the subsequent operations. With most material the following method is both rapid and accurate. The decomposition of the ore may sometimes be varied advantageously by the addition of a little hydrofluoric acid (1 ml.), to attack silica, or a small piece of filter paper to act as a reducing agent, or both. These additions are usually quite unnecessary.

B. Interfering Elements

The precipitation of tungstic acid by cinchonine will carry down small amounts of molybdenum, vanadium, antimony, phosphorus, tin, etc., which will be extracted with the tungsten by sodium carbonate. The interfering elements carried through the analysis will be small in the usual analysis and are compensated by the losses of tungsten due to the presence of alkalies.

C. Procedure

a. Weigh 0.5 gram of the very finely ground ore into an 8-oz. flask ("copper-flask"). Add 3 grams of anhydrous sodium sulfate and 5 ml. of strong sulfuric acid. Heat over a free flame, preferably with the flask in a holder, until all the free acid is expelled and the mixture reduced to a red-hot melt. Continue the fusion until the decomposition is complete. By holding the flask at an angle, so that most of the heat is on the curve just above the bottom, the bottom is prevented from bulging. Give the flask a slight circular motion during the heating. Rotate it while cooling, so as to distribute the

melt around the sides, and thus avoiding cracking. The decomposition is usually very quickly effected without any material injury to the flask. A Pyrex flask is preferred.

b. When the melt is cool, add 20 ml. of hot water, 20 ml. of strong hydrochloric acid, and 5 ml. of strong nitric acid. Boil until the bulk is reduced to about 10 ml. Add 25 ml. of hot water and 3 ml. of cinchonine solution, and cool under the tap to room temperature or cooler.

The cinchonine solution is made by dissolving 25 grams of cinchonine in 200 ml. of 1 : 1 hydrochloric acid.

c. Filter the cold mixture through a 9-cm. filter, returning the first portion if at all cloudy. The flask may be washed out with cold water while the filter still contains liquid, if the washing is done quickly. It must be remembered, however, that cold water alone, with no cinchonine present, will soon cause a cloudy filtrate. Wash filter and precipitate twice with dilute cinchonine solution (5 ml. of the above solution diluted to 100 ml.) contained in a small wash bottle. The flask may retain a little WO_3 adhering to the sides.

d. Spread the filter carefully on a watch glass and wash the precipitate, through a funnel, back into the flask with hot water, using as little as possible. Pour about 1 ml. of ammonia upon the filter in the watch glass, and set the whole on a water bath to dry.

Add 1 gram of sodium carbonate to the mixture in the flask and boil to small bulk while the filter is drying. Refold the dry filter in the original creases and replace in the funnel. Rub up any adhering residue on the watch glass with a little water and wash through the filter into a clean flask like the first. Pour the concentrated liquid in the original flask through the filter and wash out the flask with hot water. Now pour a little ammonia into the washed flask, add about 50 ml. of hot water, and use this solution to wash the filter at least ten times, with about 5 ml. each time.

e. Boil the filtrate to small bulk. This will expel all the ammonia. Add 2 grams of anhydrous sodium sulfate and (cautiously) 5 ml. of strong sulfuric acid. Spattering may be avoided by first cooling under the tap. Boil the mixture in the flask in the original manner, as described in a, until the free acid is expelled and any carbon from the cinchonine is burned off. Cool as before, add 20

ml. of strong hydrochloric acid and 5 ml. of strong nitric acid, and boil down to about 10 ml.

Add 25 ml. of hot water and 3 ml. of cinchonine solution, and cool and filter as before, using an 11-cm. ashless filter. Before washing the filter, pour a little ammonia into the flask to dissolve adhering WO_3 , and boil the solution until all free ammonia is expelled. Now add a few drops of hydrochloric acid and about 1 ml. of the dilute cinchonine solution, and cool under the tap. Pour the cold mixture into the filter and wash out the flask quickly with cold water. Wash filter and precipitate at least ten times with the cold dilute cinchonine.

f. Transfer the washed filter and precipitate to a small weighed platinum dish and ignite until the carbon is burned off. Cool, add a few milliliters of hydrofluoric acid, and evaporate to dryness to remove any silica. Again ignite and then cool and weigh as WO_3 . Multiply the centigrams by 2 to obtain the percentage.

II. HYDROFLUORIC ACID METHOD

A. Application

This method is convenient for highly siliceous material and gives results accurate enough for most technical analyses.

B. Interfering Elements

Extraction of the tungstic acid by ammonia is preferable to that of sodium carbonate as given in the preceding method. The precipitation of tungstic acid is not quite complete by acid digestion, so that the method fails where small amounts of tungsten are in question.

C. Procedure

a. Treat 0.5 gram of the very finely powdered ore in a small platinum dish with equal parts of strong hydrochloric and hydrofluoric acids. Digest on a water bath until solution is complete, adding more of each acid from time to time if necessary. It may require from one to several hours to effect complete decomposition of the ore. Usually a perfect solution may be obtained. Any tin oxide present will be unaffected. Finally, evaporate to about 15 ml.

with an excess of hydrochloric acid. A yellow precipitate of H_2WO_4 may separate during the final evaporation, owing to the expulsion of the hydrofluoric acid that holds it in solution.

b. Transfer the solution and any precipitate to an 8-oz. flask. If some of the precipitate adheres to the dish, remove as much as possible with a rubber-tipped glass rod, and rinse into the flask with a very little hot water. If some still remains, pour a few milliliters of strong ammonia over it; cover the dish and set it aside for the time being.

To the mixture in the flask add 20 ml. of strong hydrochloric acid and 5 ml. of strong nitric acid. Boil down to about 10 ml. This will expel any remaining hydrofluoric acid and precipitate the tungsten as tungstic acid, H_2WO_4 . Dilute with 50 ml. of hot water and allow to simmer at a gentle heat for about half an hour, or until the tungstic acid has settled clear. Filter, washing well with hot water.

The tungstic acid on the filter is now to be dissolved with warm dilute ammonia and the filtrate evaporated to dryness in a weighed platinum dish. Use the same dish as before. If it already contains ammonia, added to dissolve adhering tungstic acid, see that all this is dissolved, warming if necessary, and then rinse the solution into a small beaker. Dry, ignite, and weigh the dish and place it under the funnel. Warm the ammoniacal solution in the beaker and pour it over the precipitate in the funnel. Continue to pour on more warm dilute ammonia, very slowly, so as to use as little as possible, until all the precipitate is dissolved, washing the filter with the same solution.

Evaporate the filtrate in the platinum dish on a water bath, to dryness, and then ignite the residue at a red heat. Cool and weigh as WO_3 . Multiply the weight in centigrams by 2 to obtain the percentage. If tungsten is desired, $\text{WO}_3 \times 0.793 = \text{W}$. The cold residue should be of a bright canary-yellow color.

D. Modification

This is a very good method, but it has the disadvantage of requiring a long time for the decomposition of the ore. The ore must be in the finest possible state of division. The time spent in grinding will be more than made up for later. Laboratories using the method

regularly employ a large agate mortar with pestle specially fitted to run by power.

Usually 1 gram of the agate-ground sample is taken for analysis, whatever the grade, unless it is extremely low-grade ore or tailings, when 2 grams are taken.

The method of attack by acid depends somewhat on the grade of the ore; if not over 30 per cent, it is treated directly by evaporating with about 40 ml. of aqua regia; if much above this, and always for concentrates, the assay is started with 40 to 50 ml. of hydrochloric acid alone. Starting thus, when the solution has evaporated to, say, 15 ml., about 25 ml. of aqua regia is added and the evaporation again carried on until the solution has evaporated to 15 ml.

The evaporation is conducted in a small covered beaker on a hot plate.

The beaker is now removed from the hot plate, 50 ml. of hot water is added, and the mixture is allowed to stand for twenty or thirty minutes. The nearly clear solution is now decanted through a filter, as much of the residue as possible being kept in the beaker. The residue is now washed twice by decantation; 50 ml. of hot water, containing a little hydrochloric acid, is used each time.

To the residue in the beaker add about 15 ml. of ammonia solution (made by adding 400 ml. of strong ammonia to 2000 ml. of water containing 20 ml. of strong hydrochloric acid). Warm slightly until all the liberated tungstic acid is in solution. Decant through the original filter, receiving the filtrate in a large porcelain crucible. (If the ore is low grade, platinum should always be used.) The residue is now examined for any undecomposed particles of mineral: if none are found, transfer the whole to the filter with the ammonia solution (used warm in a wash bottle). The filter is then further washed with the same solution until free from tungstic acid. Five washings of 2 or 3 ml. each will suffice, if the stream is directed around the top of the filter.

Should any undecomposed mineral be found after the first treatment with ammonia, as may sometimes happen owing to the protective action of the liberated tungstic acid, wash three times by decantation with ammonia solution, and then, instead of transferring to the filter, again treat with aqua regia, which should not be stinted in amount, even if the residue is small. Use at least 30 ml. and treat

exactly as at first, except that smaller amounts of wash solutions will suffice. The tungstic acid liberated by the second acid treatment is apparently somewhat more difficultly soluble in ammonia than the first obtained, but warming and stirring will finally cause it to dissolve. Add this solution to the main ammonia solution in the large porcelain crucible.

Evaporate to dryness in the crucible, ignite gently to expel ammonia salts, and finally over the full flame of a good Bunsen burner. Cool and weigh as WO_3 .

If the ore is low grade, the evaporation should be made in a platinum dish, and the residue, after ignition, moistened with hydrofluoric acid and again ignited before weighing as WO_3 .

URANIUM MINERALS

Mineral Name	Chemical Formula	% U	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Uraninite (pitch-blende).	Complex uranium oxide, mainly U_3O_8	25-80	Olive-green to gray or brown	9-9.7	Pb, Th, Zr, R.E.,* Ca, Fe, Ag, Cu, Si	HNO_3, H_2SO_4	$Na_2CO_3 + KNO_3$
Carnotite.....	$K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot nH_2O$	45-56	Lemon-yellow	4.5	Si, Ca, Mg, Fe	HCl	$Na_2CO_3 + KNO_3$
Torbernite.....	Hydrous copper, ura- nium phosphate	47-52	Yellowish-green to green	3.5	As, Ca, Mg, Fe, Si	HNO_3, HCl	$Na_2CO_3 + KNO_3$
Autunite.....	Hydrous calcium ura- nium phosphate	46-52	Pale yellow	3.1	Mg, Ag, Sn, Fe, Si	HNO_3	$Na_2CO_3 + KNO_3$

* Rare earth elements

Uranium occurs in a number of rare minerals as carbonate, sulfate, arsenate, phosphate, vanadate, silicate, columbate, or titanate, combined with calcium, magnesium, barium, copper, lead, bismuth, iron, sodium, potassium, or the rare earths. All the powdered minerals are yellow, green, or brown in color. Those containing the more common elements yield readily to an acid attack; those containing columbium, tantalum, and the rare earths, such as samarskite and fergusonite, require fusion for complete decomposition.

Uranium salts show characteristic colors in solution, the uranous salts giving green to bluish green solutions, and the uranyl salts giving yellow solutions.

CHAPTER XXIX

URANIUM

I. VOLUMETRIC METHOD

A. Application

The following method is applicable to all grades of uranium ores and is less time-consuming than the gravimetric method.

B. Interfering Elements

Separations are provided by the method for the chief interfering elements with the exception of tungsten, which is not ordinarily associated with uranium ores. Excessive amounts of molybdenum or chromium may result in small amounts being carried into the phosphate precipitate and later reduced with the uranium by zinc. The separation of uranium from vanadium is not quite complete, even with double precipitations, when vanadium is present in large quantities. Any vanadium left in the uranium precipitate is easily corrected for, however, after the titration of the uranium is completed.

C. Procedure

a. Treat 1 gram of the ore (or more if low grade) in a small beaker with 10 ml. of strong hydrochloric acid and 5 ml. of strong nitric acid. Allow to simmer gently over a low heat until solution is as complete as possible, and then boil to dryness. Add 3 ml. of hydrochloric acid and 5 ml. of water to the residue, and warm gently until solution is as complete as before. Now add 35 ml. of water and pass in hydrogen sulfide to precipitate the members of that group. Filter, washing with hydrogen sulfide water at least seven times, receiving the filtrate in a fairly large beaker.

b. Cover the beaker and boil off the hydrogen sulfide. Remove from the heat and add 10 ml. of H_2O_2 . Now add dry sodium carbonate in small portions until the free acid is neutralized and then

about 2 grams in excess. Boil the mixture until all CO_2 is expelled and the precipitate, on standing, settles well. At this point add about 2 ml. more H_2O_2 . Filter, washing once or twice with hot water, and reserve the filtrate, which may be allowed to boil and concentrate while waiting for the next step. Rinse the bulk of the precipitate from the filter back into the beaker, then place the beaker under the funnel and dissolve what precipitate remains on the filter with dilute (1 : 1) nitric acid, using as little as possible. Now wash the filter well with hot water, allowing all to run into the beaker containing the precipitate. Warm the mixture until the precipitate dissolves, adding more acid if necessary, then add H_2O_2 and precipitate with sodium carbonate precisely as before. Filter and wash the precipitate well with hot water. Add the filtrate to the first one, which has been concentrating, and boil the whole to a bulk of about 100 ml. Now remove from the heat (simply to prevent frothing over) and cautiously add 10 ml. of strong nitric acid, and then boil again until all the CO_2 is expelled. The solution must be clear and boiling hot for the next step.

c. Place in a large beaker about 15 grams of ammonium acetate, 5 grams of microcosmic salt, 50 to 75 ml. of water, and 5 ml. of glacial acetic acid. Place a boiling-rod in the mixture, and heat to rapid boiling. Have arranged over the beaker a funnel with the lower end drawn out so as to deliver only a fine stream. Pour the hot uranium solution through this into the boiling phosphate solution. Allow to boil a few minutes after all has run through. Now remove the beaker from the heat, cover it and allow to stand until the precipitate has settled well, and then filter. Time will be saved by pouring as much as possible of the clear liquid through the filter before disturbing the precipitate. Wash the precipitate only once, using hot water. Now rinse it back into the beaker, place the beaker under the funnel, and dissolve what remains on the filter with a little hot, dilute nitric acid. Six milliliters of 1 : 1 acid is usually sufficient. Wash the filter well with hot water, receiving all in the beaker containing the precipitate. Warm the mixture until the precipitate dissolves, and dilute to about 75 ml., if necessary. Heat to boiling, and repeat the phosphate precipitation precisely as before. The two operations will remove practically all the vanadium and leave the uranium and aluminum as phosphates. Stir in a little

paper pulp and filter through the same paper as before, washing four or five times with hot water containing a little ammonium sulfate.

d. Make a mixture, in a small beaker, of 5 ml. of strong sulfuric acid and 15 ml. of water, and heat nearly to boiling. Place a 250-ml. beaker under the funnel, and pour the hot acid mixture slowly over the precipitate on the filter. With care, it may thus be all dissolved, although the hot acid may be poured through again if necessary. Wash the filter well with hot water, but do not unduly increase the volume of liquid. This should not be allowed to much exceed 50 to 75 ml. Heat nearly to boiling and run in permanganate to a permanent deep pink color, to oxidize any organic matter present. Now add 10 grams of 20-mesh C. P. zinc and allow to stand until the action has become very slow, then add 25 ml. more water and 10 ml. more sulfuric acid. When nearly all the zinc has dissolved, filter the solution through a fresh filter, washing the filter and residue well with cold water. Receive the filtrate in a 400-ml. beaker and dilute to 200 ml. with cold water. Stir vigorously with a glass rod and allow to stand for about ten minutes so that any uranium reduced below the quadrivalent stage will be re-oxidized.

e. Titrate the cool solution with the ordinary permanganate solution used for iron until a single drop produces a pink color that lasts several seconds. The end point is very sharp, although the color may soon fade, owing, possibly, to traces of vanadium. Note the buret reading and deduct the correction required for the iron in the 10 grams of zinc used, this having been determined by a blank test. As a rule, no further correction is required, as any trace of vanadium present appears to be acted on so slowly in the cold as not to interfere seriously with obtaining a sharp end point. As a precaution, however, add 1 gram of sodium sulfite and boil the solution in the flask until all smell of SO_2 has gone, and then seven or eight minutes more. Add cold water to restore the original volume, cool to room temperature, and titrate as before. Run the above zinc blank in the same way and find the correction required for the combined iron and impurities in the sulfite. After deducting this from the last reading, the remainder, if any, may be credited to vanadium and deducted as a further correction from the uranium reading.

The iron factor of the permanganate solution multiplied by 2.514 will give the U_3O_8 factor, or multiplied by 2.132, the U factor.

Vanadium may be determined in the filtrate from the phosphate separation (c) by acidifying and treating as described in the next chapter.

II. GRAVIMETRIC METHOD

A. Application

This is probably the most accurate method for the determination of uranium, especially in complex material. It is, however, quite tedious and is not well suited for a routine technical method.

B. Interfering Elements

No elements interfere unless present in exceptional quantities.

C. Procedure

a. Treat 1 gram of the ore (or more if very low grade) in a small beaker with 10 ml. of strong hydrochloric acid and 5 ml. of strong nitric acid. Allow to simmer gently over a low heat until solution is as complete as possible, and then boil to dryness. Add 3 ml. of hydrochloric acid and 5 ml. of water to the residue, warm for a short time, occasionally agitating, then dilute with 25 ml. of hot water and filter, washing with warm water. Receive the filtrate in a small beaker.

b. Pass hydrogen sulfide into the liquid to separate copper, lead, and other metals of this group, filter, wash with hydrogen sulfide water, and boil the filtrate to expel the hydrogen sulfide. Concentrate to 100 ml. if necessary, oxidize with hydrogen peroxide (usually 10 ml.), and then neutralize with dry sodium carbonate, adding 2 or 3 grams in excess. Boil the liquid for about fifteen minutes, or until the yellowish uranium precipitate dissolves, leaving a brown precipitate which is largely iron. Filter and wash the iron precipitate once or twice with hot water, and reserve the filtrate. Dissolve the iron precipitate in the least possible amount of nitric acid (1 : 1), dilute somewhat if necessary, add 10 ml. of hydrogen peroxide, and repeat the precipitation with sodium carbonate precisely as before. Filter into the beaker containing the first filtrate. Wash well with hot water.

c. Evaporate the united filtrates from the iron precipitation to a volume of about 200 ml.; add 10 ml. of strong nitric acid and boil until all CO_2 is expelled. Neutralize the free acid with ammonia

(until a slight permanent precipitate appears), then add 4 ml. of nitric acid for each 100 ml. of liquid. Now add 10 ml. of a 20 per cent lead acetate solution and enough of a strong solution of ammonium acetate to neutralize the nitric acid present and substitute acetic acid for it. The object is to precipitate the vanadium as lead vanadate in an acetic acid solution. The ammonium acetate solution may be made by mixing 80 ml. of strong ammonia, 100 ml. of water, and 70 ml. of acetic acid 99 per cent pure.

d. Heat the liquid containing the lead vanadate precipitate on the steam bath for one hour or more, filter on a close filter, and wash with warm water. Dissolve the precipitate in the least possible quantity of hot dilute nitric acid, neutralize as before, add 3 ml. of nitric acid in excess, then 2 ml. of lead acetate solution, and repeat the precipitation of lead vanadate by adding ammonium acetate in excess. Filter and add the filtrate to the one from the first precipitation of lead vanadate. Evaporate the united filtrate from the lead vanadate to about 400 ml. Add 10 ml. of strong sulfuric acid to separate the bulk of the lead (derived from the excess of lead acetate) as PbSO_4 , and filter, washing the precipitate with cold water. Neutralize the filtrate from the PbSO_4 with ammonia and add freshly prepared $(\text{NH}_4)\text{HS}$ until the solution is yellow and the uranium and what little lead is present are precipitated as sulfides. Warm the mixture gently until the sulfides settle well. Filter and wash slightly with warm water.

e. Dissolve the precipitate in a 150-ml. beaker with hot dilute (1 : 2) nitric acid; add 5 ml. of strong sulfuric acid and evaporate until it is fuming. Cool, take up with water, boil, let the small precipitate of PbSO_4 settle until the liquid is cold, and then filter it off, washing with very dilute sulfuric acid (1 : 20).

f. Nearly neutralize the filtrate with ammonia. Have the solution cold (not warmer than 30°C.), and add powdered ammonium carbonate in about 2 grams excess. This will precipitate the aluminum and hold the uranium in solution. Let the precipitate settle, filter, and wash it with warm water. If the precipitate is bulky or at all yellow, dissolve it in a little dilute sulfuric acid and reprecipitate with ammonium carbonate as before.

g. Acidify the filtrate, or combined filtrates, from the alumina with sulfuric acid, and boil to expel CO_2 thoroughly. Make the

liquid slightly alkaline with ammonia while it is hot, and heat gently until the ammonium uranate collects and settles. Filter and wash with a very dilute solution (2 per cent) of ammonium nitrate. Do not allow the precipitate to run dry on the filter after the first washing. Dry the precipitate, ignite it in a porcelain crucible, and weigh as U_3O_8 . Dissolve the ignited residue in a little nitric acid and test it with H_2O_2 for vanadium. Only a faint brownish tint should appear, at most. Rinse the solution into a small beaker and test for alumina with ammonium carbonate. Should an appreciable amount be found it may be filtered off, ignited, weighed and deducted.

III. CUPFERRON METHOD ¹

A. Application

This method is based on the fact that uranium is precipitated quantitatively by cupferron when in a valence of four and is not affected by the reagent when in a valence of six. Owing to the voluminous precipitate formed by the reagent the procedure is especially valuable for the separation of small amounts of uranium from elements such as aluminum, phosphorus, manganese, and chromium.

B. Interfering Elements

Only elements that are precipitated by cupferron in their lower valences and not in their higher valences will interfere. Of this class are antimony, chromium, and possibly tungsten.

C. Procedure

a. Fuse 0.5 gram of the finely ground ore in a platinum crucible with 5 grams of sodium carbonate and a little potassium nitrate. In the presence of elements injurious to platinum an iron or nickel crucible may be used and sodium peroxide substituted for the potassium nitrate; or an acid digestion may be used, the sample being treated as in I, C, a and b, till the filtrate from the sodium carbonate precipitation is obtained. If the fusion method is used, extract the melt with about 50 ml. of water by boiling, then filter, and wash once with a hot 5 per cent sodium carbonate solution. Dry

¹ G. E. F. Lundell and H. B. Knowles, *Ind. Eng. Chem.*, **12**, 344, 1920; J. A. Holladay and T. R. Cunningham, *Trans. Am. Electrochem. Soc.*, **43**, 329, 1923.

the paper and residue, ignite carefully in the original platinum crucible, and repeat the fusion and extraction. Combine the two filtrates in a 400-ml. beaker.

b. Cover the beaker; neutralize with sulfuric acid (1 : 1) and add 20 ml. in excess. Boil the solution down to a volume of 100 ml. remove from the plate, and add a solution of potassium permanganate, until pink, to make sure that the solution is completely oxidized. Add 5 ml. of hydrogen peroxide to decolorize the permanganate and reduce any chromium, if present, to a valence of three.

c. Cool the solution in the refrigerator, and add slowly, with stirring, a cool 6 per cent water solution of cupferron, until the continued addition produces a white flashing precipitate that rapidly disperses, then a few milliliters in excess. Stir in a little paper pulp and filter on a rapid paper. Wash with a cold solution of 1 per cent sulfuric acid containing a little of the reagent.

d. Evaporate the filtrate down till it starts to turn brown from carbon, then make repeated additions of nitric acid till the carbon is completely burnt off, and finally take to strong fumes of sulfuric acid. Cool. Wash down the sides of the beaker with a fine stream of water, and again take to fumes on the hot plate. Cool and dilute to 60 ml.

e. Heat the solution nearly to boiling; remove from the plate and add about 7 grams of 20-mesh C. P. zinc. Allow to stand until the action has become very slow and filter through a little cotton pressed into the funnel. Wash with cold water.

f. Add 10 ml. of sulfuric acid, dilute to 150 ml., and cool in the refrigerator. Precipitate the uranium with cupferron as described in c, add a little paper pulp, and filter on an ashless paper. Remove the excess moisture by suction, and transfer the filter and contents to a porcelain crucible. Dry carefully on the hot plate, char, and ignite in a muffle at bright heat with free access to the air. Cool and weigh as U_3O_8 . The purity of the compound may be checked volumetrically.

VANADIUM MINERALS

Mineral Name	Chemical Formula	% V	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Vanadinite	$3 \text{ Pb}_3\text{V}_2\text{O}_8 \cdot \text{PbCl}_2$	10.9	White to yellowish	7.0	Zn, Cu, Mo, P, As	HCl, HNO_3	$\text{Na}_2\text{CO}_3 + \text{KNO}_3$, Na_2O_2
Carnotite	$\text{K}_2\text{O} \cdot 2 \text{ UO}_3 \cdot \text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$	10-11	Lemon-yellow	4.5	Si, Ca, Mg, Fe	HCl	Same as above
Patronite	$\text{VS}_4 \cdot n\text{S}$	16-29	Gray to black	2.5	Si, Fe, Ni, Mo	HNO_3	
Descloizite	$4 (\text{PbZn})\text{O} \cdot \text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$	11-12	Orange to brownish red	6.0	Si, Fe, Mo, Cu	HNO_3	Same as above
Roscoelite	Hydrous K, Al, V silicate	12-16	White to brown, micaceous	3.0	Fe, Mn, Ca, Mg, Na		Same as above

The vanadium minerals in pulverized form are for the most part yellow to orange, brown, or green, and are usually broken up by an acid treatment. Vanadium occurs in small amounts in a great many ores and rocks, such as clays, limestones, coals, micas, amphiboles, and pyroxenes. Vanadium salts give colors in acid solutions from violet to green to blue to yellow, orange, or red, according to their valence and concentration.

CHAPTER XXX

VANADIUM

I. VOLUMETRIC METHOD¹

A. Application

The method is applicable to all ores of vanadium. In certain cases the method of decomposition may be changed to advantage either to an alkaline oxidizing fusion, or a direct oxidation by perchloric acid as recommended for steels by Willard and Young.

B. Interfering Elements

In the method as given, tungsten is the only interfering element. The same is true of reduction with hydrochloric acid. When reduction is accomplished by sulfur dioxide, iron, antimony, arsenic, copper, and chromium should be removed.

C. Procedure

a. Weigh 0.5 gram (or 1 gram if of very low grade) of the finely ground ore into an 8-oz. flask. Add 5 grams of anhydrous sodium sulfate, 5-6 ml. of strong sulfuric acid, and about as much hydrofluoric acid as can be held in an ordinary platinum crucible cover. (The hydrofluoric acid is advisable, although not always necessary.) Heat over a strong free flame, (with the flask in a holder) nearly to a melt. Allow to cool while distributing the mass around the sides of the flask. This prevents the solidifying cake from cracking the flask and also facilitates subsequent solution.

b. When the flask is sufficiently cool, add 50 ml. of cold water and 10 ml. of strong sulfuric acid, and boil to dissolve everything soluble. Now, add 7 ml. of syrupy phosphoric acid, and then, from a buret, run potassium permanganate solution into the hot liquid until a decided red color is obtained that persists after boiling again.

¹ Adapted from the method for the determination of chromium and vanadium in steel by H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, 6, 48, 1934.

Use the same permanganate as will be employed in the subsequent titration.

c. Transfer the solution to a 400-ml. beaker, dilute to 250 ml., and allow to come to room temperature. Add an excess of ferrous sulfate or ferrous ammonium sulfate (either solid or in solution) until all the vanadium (and chromium when present) is reduced or until a drop of the solution gives a strong blue color with a drop of potassium ferricyanide solution. Add two or three drops of 0.025 *M* ortho-phenthroline ferrous complex² and then 0.10 *N* potassium permanganate solution from a buret until the solution just changes from pink to green. Add 20 grams of sodium acetate crystals to the solution, warm the solution to just 50° C., and then add one more drop of the indicator.

d. Titrate the solution with 0.10 *N* permanganate solution till the pink of the indicator changes to a clear green, the number of milliliters used representing the amount necessary to oxidize the vanadium from a valence of four to a valence of five. One milliliter of 0.10 *N* permanganate is equivalent to 0.0051 gram of vanadium or 0.0091 gram of V_2O_5 .

D. Modifications

a. The solution may be titrated in hot solution as follows:

Transfer the hot solution from b to a 400-ml. beaker and dilute to 200 ml. with hot water. Have ready a spot plate, and place a drop of the ferricyanide solution in each of the depressions.

Using a small pipet, add the ferrous solution in small portions at a time, very cautiously, finally drop by drop, to the hot liquid in the beaker, testing after each addition, until a drop of the vanadium solution, taken up on a glass rod and allowed to fall on a ferricyanide test, produces a blue color.

The ferrous solution first decolorizes the permanganate, then reduces the V_2O_5 to V_2O_4 , and finally, in slight excess, it shows a blue color with the ferricyanide. Try to avoid an unnecessary excess of the ferrous solution. The excess of ferrous salt must now be oxidized to ferric. Run the regular permanganate solution in from the buret until the ferricyanide test fails to develop a blue tinge after

² Walden, Hammett and Chapman, *J. Am. Chem. Soc.*, 53, 3908, 1931; 55, 2649, 1933.

standing about half a minute. This should be done as carefully as in a regular titration, as faint tinges of color develop slowly and should be waited for. Toward the last the permanganate should be added a drop at a time.

When no blue tinge develops in about half a minute the oxidation of the excess of ferrous iron may be considered complete. Titrate the still hot liquid with standard potassium permanganate solution until a very faint pink tinge is obtained that persists for at least a minute, when it may change to brownish.

b. *Hamner's*³ *Method*. To the solution obtained in C, b, in a volume of 200 ml. and cooled to room temperature, add a slight excess of ferrous sulfate as usual. Oxidize the excess by stirring in 1 gram of ammonium persulfate and allowing to stand with occasional agitation until a drop tested with ferricyanide solution no longer gives a blue color. Titrate the reduced vanadium in the usual manner.

c. *Hillebrand's*⁴ *Method*. The vanadium is reduced by passing sulfur dioxide through the dilute sulfuric acid solution and boiling off the excess. The reduced solution is titrated with permanganate as usual. A number of elements interfere, necessitating preliminary separations of the hydrogen sulfide and sodium carbonate groups.

d. *Campagne's*⁵ *Method*. Weigh 1-5 grams of the finely ground ore into a 16-oz. flask. Add 30 ml. of 1 : 1 sulfuric acid and boil to fumes. The insoluble gangue is likely to make the mixture bump badly. Use a boiling-rod, agitate the flask frequently, and, if necessary, run down by hand. Maintain at fuming point for ten minutes. Allow to cool and then dilute to about 75 ml. If the bumping was bad, filter at this point and then return the liquid to the flask. Heat somewhat, and add sufficient powdered potassium permanganate to produce a strong pink color that persists on boiling. This destroys any organic matter.

Cool slightly and add 50 ml. of strong hydrochloric acid. Boil gently, nearly to fumes. About 15 ml. of strong sulfuric acid should still be present to keep all salts in solution. Again cool sufficiently

³ J. L. Hamner, *Met. Chem. Eng.*, 17, 206, 1917; Hillebrand and Lundell, *Applied Inorganic Analysis*, John Wiley & Sons, Inc., 1929.

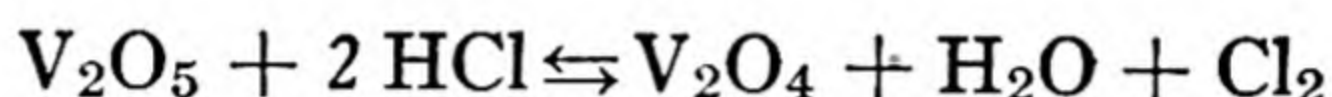
⁴ W. F. Hillebrand, *U. S. Geol. Survey Bull.* 700, 1919.

⁵ Em. Campagne, *Compt. rend.*, 137, 570, 1903.

and add 25 ml. more of hydrochloric acid. Boil nearly to fumes once more and note the color, which, in the absence of much iron, should be pure blue. If greenish (unless much iron is present), repeat the boiling with more hydrochloric acid until blue. Organic matter, unless previously destroyed, would make trouble here.

Finally, continue the boiling to strong fumes. Fume about a minute and then allow to cool completely. Dilute to about 200 ml. with cold water, heat nearly to boiling, and titrate to the usual pink tinge with standard potassium permanganate solution.

The basis of this method is, of course, the reduction of V_2O_5 to V_2O_4 by boiling with hydrochloric acid. This appears to depend upon the reaction



The free chlorine naturally makes the reaction easily reversible. Some of the chlorine reacts to oxidize the V_2O_4 again, and some is lost by volatilization. Owing to this loss of chlorine, the amount of reduction gradually increases by the continued action of more hydrochloric acid until it is practically complete. This is why so much hydrochloric acid and such long boiling are required.

ZINC MINERALS

Mineral Name	Chemical Formula	% Zn	Distinctive Properties of the Mineral in Powdered Form	Sp. Gr.	Associated Elements	Decomposed by	
						Acid	Flux
Sphalerite	ZnS	67.0	White, yellow or brown, resinous	4.0	Pb, Fe, Cu, Mn, Ag, Sb, Cd, Hg, Ca, Ba, F	HCl, HNO ₃	
Smithsonite . . .	ZnCO ₃	52.0	White or tinted	4.4	Fe, Mn, Co, Ca, Mg, Cd, Pb, Cu	HCl, HNO ₃	
Calamine	2 ZnO · SiO ₂ · H ₂ O	54.1	White or tinted	3.5	Same as above	Incompletely	Na ₂ CO ₃
Zincite	ZnO	80.3	Orange-yellow to brownish	5.5	Mn, Fe, Ca, Mg, Pb, As, P, S, Cd	HCl, HNO ₃	Na ₂ CO ₃
Franklinite . . .	(FeZnMn)O · (FeMn) ₂ O ₃	Variable	Reddish brown to black, metallic luster	5.1	Ca, Mg, Pb, As, P, S, Cd	HCl	Na ₂ CO ₃
Willemite	2 ZnO · SiO ₂	58.5	White to grayish	4.0	Mn, Fe, Ca, Mg, Pb, As, P, S, Cd	Incompletely	Na ₂ CO ₃

No difficulty is ordinarily encountered in the decomposition of zinc ores. Sphalerite is usually present in a sulfide ore when the ore liberates fumes of hydrogen sulfide rapidly on treatment with hydrochloric acid. As zinc is a common constituent of a large number of rocks, the analyses of some materials will require fusion of the insoluble matter.

Zinc gives few indications of its presence in the course of an ordinary analysis, and unless special tests are made it may frequently cause an error in determinations of elements such as calcium, magnesium, uranium, and the alkalis.

CHAPTER XXXI

ZINC

I. LOW'S ROUTINE METHOD

A. Application

The following method for the technical estimation of zinc in ores, etc., is of general but not of universal application. Ordinarily, however, almost the only source of trouble likely to be encountered is the preliminary decomposition of the ore. The method as described is applicable to the usual run of mixed sulfide ores and many oxidized ores. When the decomposition fails or is doubtful, the operator must note the fact and apply the proper remedy. Some ores require a more or less prolonged treatment with hydrochloric acid, to insure complete decomposition of oxides, before adding nitric acid. Ores that gelatinize should be mixed with a little water before any acid is added, and then the acid should be added while the flask is being agitated, to prevent setting or caking. This is to be followed by occasional agitation during decomposition.

B. Interfering Elements

Of the elements precipitated by potassium ferrocyanide and not removed by ammonium hydroxide, copper and manganese are most often troublesome. This method takes care of these two satisfactorily but does not prevent interference by cadmium, cobalt, nickel, tungsten, molybdenum, vanadium, or uranium, when the last is present with vanadium.

Cadmium is not completely precipitated by hydrogen sulfide from a hydrochloric acid solution containing considerable alkali chloride. In the regular method (and likewise the alternate and test-lead methods), therefore, cadmium is to a greater or less extent counted as zinc, small amounts not being precipitated at all by the hydrogen sulfide.

Arsenic, when present in large amount, may make trouble by retaining iron in the ammoniacal solution filtered from the residue. No attention need be paid to arsenic unless its presence in excess is indicated. A large amount of gelatinous silica may hold some zinc mechanically and thus render its complete extraction and the thorough washing of the residue more difficult. The partial dehydration obtained by following the regular method is usually quite sufficient to overcome this trouble. When hydrofluoric acid has been used in the decomposition of the ore no appreciable amount of gelatinous silica is likely to be found.

C. Procedure

a. Weigh 0.5 gram of the ore into a 250-ml. beaker. Add 5 ml. of strong hydrochloric acid and 10 ml. of strong nitric acid. It is often highly advantageous to add also about 2 ml. of hydrofluoric acid—as much as can be held in the hollow of an ordinary platinum crucible cover. This tends to prevent any possible trouble from gelatinous silica. One must be certain, however, when this acid is used, that the glassware contains no zinc.

Boil gently until only a few milliliters of liquid remain, but endeavor not to take to dryness. Remove from the heat, add 15 ml. of strong nitric acid saturated with potassium chlorate, and take just to dryness. Hard dryness is unnecessary except when gelatinous silica is present, and even then there should be no overheating or fusing of the salts. With other ores it is sufficient to run just to dryness and remove at once from the heat.

b. As soon as the beaker is sufficiently cool, add 35 ml. of a prepared ammoniacal solution and heat to boiling. This solution is made by dissolving 200 grams of commercial ammonium chloride in a mixture of 500 ml. of strong ammonia (sp. gr. 0.90) and 50 ml. of water.

Boil the contents of the beaker very gently for a minute or two, or until disintegration of the residue is complete (avoiding hard boiling and loss of ammonia), and then add saturated bromine water and continue the boiling for a short time.

The amount of bromine water to add depends upon the quantity of manganese apparently present, as indicated by the deep brown color of the dry residue. All the manganese is originally precipi-

tated by the mixture of nitric acid and potassium chlorate, but, on evaporating to dryness, some of the manganese is again reduced to the protoxide form and becomes more or less soluble. With ores showing little or no manganese, 10 ml. of saturated bromine water is sufficient, and 25 ml. will usually suffice under any circumstances.

c. Filter the hot solution through an 11-cm. filter into a 400-ml. beaker. Wash out the beaker with hot water. A slight adhering residue may be disregarded; a larger residue that cannot be removed with a rubber-tipped rod may be treated as follows: Add 2 or 3 ml. of strong hydrochloric acid to dissolve it, and then, without diluting the solution, add 5 ml., or an excess, of strong ammonia, and rinse into the filter. Any traces of manganese not precipitated by the ammonia are usually negligible.

Wash the residue on the filter ten times with a nearly boiling ammonium chloride mixture (dissolve 100 grams of commercial ammonium chloride in water, add 50 ml. of strong ammonia, and dilute to 1 liter).

d. Add a little litmus solution to the filtrate as an indicator, and then cautiously neutralize with strong hydrochloric acid. Be very particular with the neutralization, and then add 3 ml. of hydrochloric acid in excess. When sufficient copper is present to act as an indicator, the litmus may be dispensed with.

Dilute the liquid, if necessary, to about 250 ml., with hot water, heat nearly to boiling, and then add 50 ml. of saturated hydrogen sulfide water. The mixture is now ready for titration. If the final bulk of the liquid happens to be considerably larger than prescribed it will have no material influence on the zinc result.

e. Titrate with the ferrocyanide solution as follows: Pour about two-thirds of the zinc solution from the flask into a 400-ml. beaker. Run the ferrocyanide solution from the buret into this portion, a few milliliters at a time, until a drop, when removed and tested on a porcelain plate with a drop of a 15 per cent solution of uranium nitrate, shows a brown tinge. Now add more of the zinc solution from the flask and continue the titration more cautiously until the end point is again passed. Proceed thus, adding more of the reserved portion in such amounts as may appear advisable, passing the end point each time with greater caution. Finally, add the last of the reserved portion, and then, to save rinsing out the flask, pour

a large part of the solution back into it again and then empty it once more into the beaker. From this point finish the titration very carefully, ordinarily by testing after each addition of 2 drops.

When the final brown tinge is obtained, note the reading of the buret, and then wait a minute or two and observe whether one or more of the preceding tests does not also develop a color. The end point is always passed by a test or two, and the buret reading must be corrected accordingly. Deduct for as many tests as show a color and for 1 drop additional, since 2 drops are required to show a test when no zinc is present.

Multiply the number of milliliters used by the percentage value of 1 ml. to obtain the percentage of zinc in the ore.

Ordinarily, any sulfides precipitated by the hydrogen sulfide water need not be filtered off, as the discoloration produced by even 10 per cent of copper, for instance, does not too badly mask the uranium test. With a large amount of copper present the procedure may be as follows: After adding an excess of 3 ml. of strong hydrochloric acid to the filtrate and diluting it to about 200 ml. with hot water, pass in hydrogen sulfide gas to saturation. Filter through an 11-cm. filter, and wash the precipitate thoroughly with hot water. If a little copper oxidizes and runs into the filtrate it will do no harm, as it is immediately reprecipitated as sulfide. Heat the filtrate, which should have a final volume of about 250 ml., nearly to boiling, and titrate as usual.

D. Modifications

a. *Alternate Method for Material Low in Manganese.* Treat 0.5 gram in a 250-ml. beaker with 5 ml. of hydrochloric and 10 ml. of nitric acids and evaporate to dryness. A few milliliters of sulfuric acid is not objectionable when gelatinous silica separates. Cool, add 10 grams of ammonium chloride and 5 ml. of hydrochloric acid, and wash down the inside of the beaker with a little water. Evaporate to pastiness, add 50 ml. of water, and warm until all soluble salts are in solution. Add ammonium hydroxide in about 5-ml. excess, then 20 ml. of saturated bromine water, and boil for a few minutes. Filter and finish as in C, d, and e.

b. *Test-lead Method.* This procedure is satisfactory for certain types of ores which are relatively free of members of the hydro-

gen sulfide group. The filtrate obtained in C, c, or D, a, is made slightly acid with hydrochloric acid, using methyl orange as an indicator. Add about 20 grams of granulated test lead, cover the beaker, and boil until the solution is colorless and any copper present is precipitated on the lead. Decant the boiling hot solution into another 400-ml. beaker and wash twice by decantation with hot water. Dilute to 250 ml. with hot water, add 3 ml. of hydrochloric acid, and titrate.

The titration may be done very rapidly by adding a trace of ferrous sulfate to the solution. This causes a light blue color to form owing to the presence of the ferricyanide in the standard ferrocyanide solution. Proceed steadily with the addition of the ferrocyanide solution, not too rapidly, and stirring the zinc solution vigorously. When the end point is reached the solution brightens or flashes as the blue color gives way to a light greenish white color. With a little practice this is easily seen, but it is not so satisfactory as the uranium indicator for titration of only a few milliliters or above 50 ml.

If the unknown solution turns green on the addition of the ferrocyanide, cobalt, nickel, or vanadium is likely to be present; if brown, tungsten, molybdenum, uranium, or unremoved copper may be expected. In any event, if the precipitate formed is not white or light blue, the result will be high and preliminary separations are required.

II. MODIFIED WARING METHOD¹

A. Application

This method depends upon the separation of the zinc from interfering elements by means of hydrogen sulfide. Though applicable to almost any type of material it is time-consuming and best adapted to complex ores.

B. Interfering Elements

The only interfering elements under ordinary conditions are cadmium and mercury. Cadmium may be removed by hydrogen sulfide by modifying the conditions to those described in the chapter on cadmium. Mercury must be removed at the start of the analysis.

¹ W. G. Waring, *J. Am. Chem. Soc.*, 29, 265, 1907.

C. Procedure

a. Calamine, willimite, franklinite, blende, and other soluble minerals, or ores containing them, are decomposed by hydrochloric acid or aqua regia, with subsequent treatment and evaporation with an excess of hydrochloric or sulfuric acid to eliminate nitrous compounds thoroughly. If zinc spinels or aluminates are present, the insoluble residue must be fused with a mixture of sodium carbonate and borax glass, the fused mass dissolved, and the solution added to the main one. If much silica is present, spinels are decomposed by fusion with sodium carbonate in a platinum crucible, any lead sulfate present having been extracted by ammonium acetate. In the absence of silica or boric acid, the spinels cannot be decomposed by fusion with sodium carbonate alone, but they can be decomposed by prolonged fusion with an alkali bisulfate. Silicates, such as cinders from oxide furnaces, unchilled slags, and some natural silicates undecomposable by acids must be fluxed or sintered with sodium carbonate before treatment with acid.

After the weighed sample has been decomposed by acids alone, or aided by fusion, as circumstances may require, all the zinc is to be brought into solution as sulfate. If nitric acid was used in the decomposition, all traces of it must be expelled by evaporation with hydrochloric and sulfuric acids successively, or by two evaporations with sulfuric acid, finally to abundant evolution of SO_3 fumes. Dissolve the mass in 25 to 40 ml. of water and add sufficient sulfuric acid to bring the free acid in the solution up to 10 or 15 per cent.

b. Introduce a piece of heavy sheet aluminum and boil ten minutes, or to complete reduction. Filter, and wash through a filter containing a piece of aluminum, into a beaker containing a stirring-rod or strip of the same metal; cool, add a drop of methyl orange, and neutralize carefully with sodium bicarbonate to a light straw color. Add, dropwise, dilute formic acid (20 per cent strength) until the pink color is just restored, then 5 drops more. (Dilute hydrochloric acid, 1 part strong acid to 6 parts water, may be substituted for formic acid when ammonium thiocyanate is to be introduced.) Dilute to about 100 ml. for each 0.1 gram of zinc possibly present; if much iron is present, add 2 to 4 grams ammonium thiocyanate; remove the strip of aluminum, heat nearly to boiling, and saturate with hydrogen sulfide. Allow the pure white zinc sulfide

to subside for a few minutes, then filter and wash with hot water. Place the paper and precipitate in a small beaker, and dissolve the zinc sulfide with 50 ml. of 1 : 1 hydrochloric acid by boiling. Add a little litmus solution or paper, neutralize with ammonia, and then reacidify with 3 ml. excess of hydrochloric acid. Transfer to a 400-ml. beaker, dilute to 250 ml., and titrate hot, as in I, C, d, and e.

III. HILLS' METHOD ²

A. Application

This method is especially adapted to the determination of small amounts of zinc in the presence of large amounts of iron, manganese, aluminum, or elements that give a bulky precipitate with ammonium hydroxide.

B. Interfering Elements

A small amount of iron or manganese, in a manganese ore, will accompany the sulfide precipitate, and may be separated by the usual methods. The amount is so small as to cause no serious difficulty. Lead and copper are precipitated quantitatively with the zinc. This separation may be found useful for the determination of lead and copper in low-grade products, such as mill tailings. Cadmium, cobalt, and molybdenum interfere.

C. Procedure

a. Weigh 5 grams of material into a 400-ml. beaker and decompose with hydrochloric acid, with the addition of nitric acid if sulfides are present. After decomposition, evaporate to dryness and bake. Cool, add about 10 ml. of hydrochloric acid, and warm gently until all soluble matter is dissolved. Filter, and wash the insoluble material free from chlorides.

b. Neutralize the excess hydrochloric acid with ammonium hydroxide, leaving the solution sufficiently acid to prevent hydrolysis of the iron. Add an excess of a sodium citrate solution, prepared by dissolving 1 pound (453.6 grams) of sodium citrate and 20 grams of citric acid in sufficient water to make 1 liter of solution. It is

² F. G. Hills, *Ind. Eng. Chem., Anal. Ed.*, 5, 201, 1933; *The Technical Analysis of Ores and Metallurgical Products*, Chemical Publishing Co., 1937, p. 177; H. A. Bright, *Bur. Standards J. Research*, 12, 388, 1934.

not possible to state the exact quantity of sodium citrate which will meet all conditions, as this depends upon the amount of iron and on the excess hydrochloric acid present. In general from 20 to 50 ml. of the solution is required. There should be enough hydrochloric acid to prevent the formation of any precipitate upon the addition of the sodium citrate solution, and enough sodium citrate solution to react with the excess hydrochloric acid.

Dilute to 250 to 300 ml., and pass hydrogen sulfide through the cold solution until it is thoroughly saturated and the precipitate coagulates.

c. Filter and dissolve the precipitate with hot dilute nitric acid into the beaker used for the precipitation. Evaporate to dryness and bake. Cool, dissolve the residue in hydrochloric acid, add about 6 grams of ammonium chloride, and proceed as in I, C, b, c, d, and e.

CHAPTER XXXII

SELECTIVE ANALYSIS

The metallurgical treatment of ores often requires knowledge not only of the total amount of an element present but also of the amounts of the element in its different combinations or mineralogical forms. The methods of analysis required for this information are based on differences in resolution or solubility of the two or more mineral components in a selected reagent.

I. AVAILABLE LIME

Smelters regard the calcium contained in calcium fluoride as of no value as a flux, claiming that it passes through the furnaces unaltered, without combining with the fluxes used. In paying for the lime in an ore, only that which is not combined with fluorine is taken into consideration and is called "available lime." The following method will give all the CaO contained in the ore as carbonate and also as sulfate, unless the sulfate is in large amount. Calcium combined as fluoride or silicate remains practically undissolved by the acetic acid. The silicate is usually small in amount, and the calcium so combined is, in fact, regarded as no more "available" than that existing as fluoride.

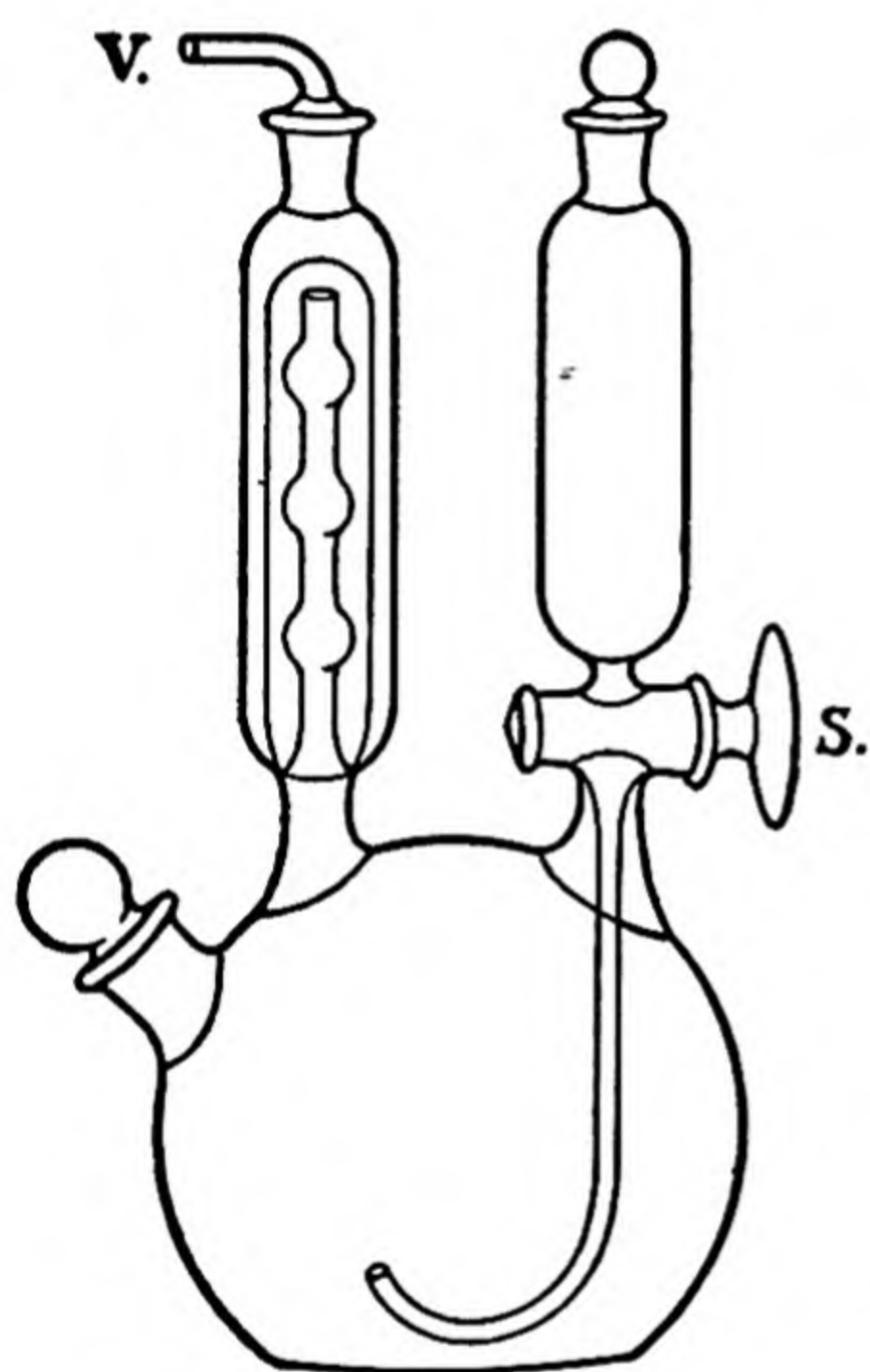
Put 0.5 gram of ore in a 250-ml. beaker, moisten with water, add 5 ml. of 80 per cent acetic acid, and boil nearly to pastiness. Take up in about 30 ml. of equal parts of 80 per cent acetic acid and water, and boil gently for a few minutes. To remove lead, which is frequently present, add 2 ml. of a saturated solution of potassium dichromate just previous to this boiling. Filter, washing with hot water. To the filtrate add about 20 ml. of saturated bromine water and then (cautiously) make alkaline with ammonia and heat to boiling. It is generally best now to add more bromine water and continue the heating for a short time to make sure of the precipitation of all manganese. Finally, boil off all the free ammonia,

allow to settle somewhat, and filter and wash. Finish the determination as described under **Calcium, I, C, d, and e.**

II. CARBONATES

The determination of carbonates by the loss of weight of the sample due to the evolution of the CO_2 by acids is quick and convenient for most purposes.

Place 0.5 gram of the sample in the bottom of the Schroetter alkalimeter, shown in Fig. 18, by means of a small funnel. Carefully fill the absorption tube half full with concentrated sulfuric



acid containing a little dissolved silver sulfate, and, after making sure the stopcock **S** is closed, fill the acid tube with 1 : 1 hydrochloric acid. When pyrolusite is present in the material use 1 : 1 nitric acid to prevent the formation of chlorine. Replace all the stoppers, and weigh the completely charged apparatus.

Remove the stopper on the acid tube and open the stopcock **S** slowly so as to allow the acid to enter the lower compartment only fast enough to generate a slow stream of bubbles through the sulfuric acid.

When the reaction has subsided, warm the bottom of the alkalimeter and apply a gentle suction to the vent **V** until the action of the acid is complete. Cool to the same temperature as before, replace the stopper to the acid tube, and again weigh. The loss in weight represents the CO_2 in the sample.

III. OXIDIZED COPPER¹

This method provides a separation of the copper in oxidized form as in cuprite, tenorite, malachite, and chrysocolla from that in the sulfide form as in chalcocite, covellite, and chalcopyrite.

Place 2 grams of pulp, ground to fineness of 100- to 150-mesh,

¹ Van Barneveld and Leaver, *Met. Chem. Eng.*, Feb. 15, 1918.

in a bottle, and add 100 ml. of a 3 per cent solution of sulfur dioxide. Seal the bottle and agitate by rolling for one-half to two hours. Filter; wash the residue with sulfur dioxide solution; add the washings to the filtrate, which will contain in solution all oxides, carbonates, and silicates of copper, and all metallic copper. Determine copper in the filtrate, by any of the methods given in the chapter on copper, after boiling to remove the SO_2 .

IV. VALUATION OF FLUORSPAR ²

The usual determinations are calcium carbonate, silica, and calcium fluoride, although other constituents are sometimes required.

Calcium Carbonate. Place 1 gram of the finely powdered sample in a small Erlenmeyer flask, add 10 ml. of 10 per cent acetic acid, and insert a short-stemmed funnel in the neck of the flask as a splash trap. Heat the mixture for one hour on a water bath, agitating from time to time. The calcium carbonate is decomposed and may be dissolved out as the soluble acetate, while calcium fluoride and silica are practically unaffected. Filter the solution through a 7-cm. ashless filter, and wash the residue four times with warm water. Ignite filter and contents in a weighed platinum crucible at as low a temperature as will burn the filter completely. The loss of weight minus 0.0015 gram (the amount of calcium fluoride soluble in acetic acid under the conditions named) is reported as calcium carbonate.

Silica. Mix the residue in the platinum crucible with about 1 gram of yellow mercuric oxide, in the form of an emulsion in water, breaking up any hard lumps that may have formed. Evaporate the mixture to dryness, heat to dull redness, then cool and weigh. The mercuric oxide oxidizes any sulfides that may be present. Add about 2 ml. of hydrofluoric acid and evaporate to dryness. Repeat this process twice (performing it three times in all), to insure complete expulsion of silica (as SiF_4). Now add a few drops of hydrofluoric acid, a little macerated filter paper, and then a few drops of ammonium hydroxide, to precipitate the iron. Evaporate to dryness, ignite to dull redness, cool, and weigh. Report the loss from the previous weighing as silica.

² Dr. E. Biddel, *J. Am. Chem. Soc.*, 4, 201, 1912; 6, 265, 1914.

Calcium Fluoride. Treat the residue with 2 ml. of hydrofluoric acid and 10 drops of nitric acid (to decompose the oxides), cover the crucible, and place on a moderately warm water bath for thirty minutes. Now remove the lid and evaporate to dryness. Repeat the evaporation with hydrofluoric acid to insure the transposition of the nitrates to fluorides. If the residue is still colored, repeat the evaporation a third time. Finally, add a few drops of hydrofluoric acid and 10 ml. of ammonium acetate solution. The acetate solution is made by neutralizing 40 ml. of 80 per cent acetic acid with strong ammonia, adding 2 grams of citric acid, and making the mixture up to 100 ml. with strong ammonium hydroxide. Digest the mixture in the crucible for thirty minutes on a boiling water bath, then filter, washing first with water containing a small amount of ammonium acetate, and finally with pure hot water. (Several washings by decantation are advisable.) Ignite the residue in the same crucible as before, and weigh as calcium fluoride. To this weight add 0.0022 gram to compensate for loss of CaF_2 .

Pure calcium fluoride is white. To test the purity of the residue, add 2 ml. of sulfuric acid and heat to fumes to decompose the fluoride, then add an additional milliliter of sulfuric acid and heat to complete dryness, expelling all the free acid. Weigh the residue as calcium sulfate, which, on calculation, should check the calcium fluoride previously weighed. Now fuse with sodium carbonate and treat the mass, after cooling, with dilute hydrochloric acid in excess. If barium is present the solution will be cloudy from barium sulfate.

V. FERROUS IRON ³

Place 0.5 gram of the powdered material in a platinum crucible and moisten with freshly boiled and cooled water. Add 15 ml. of sulfuric acid (1 : 2), cover with a close-fitting platinum lid, and heat rapidly till almost boiling. Carefully move the lid to the side just far enough to introduce 5 ml. of hydrofluoric acid and quickly cover again, and allow to boil gently for 10 minutes without interruption. While this is in progress, to 200 ml. of the freshly boiled and cooled water in a 400-ml. beaker, add 15 ml. of the (1 : 2) sulfuric acid and 10 ml. of a saturated solution of boric acid. Immerse the platinum crucible and contents in the solution in the

³ J. P. Cooke, *Am. J. Sci.*, (2) 44, 347, 1867; J. H. Pratt, *Am. J. Sci.*, (3) 48, 149, 1894; O. L. Barnebey, *J. Am. Chem. Soc.*, 37, 1481, 1915.

beaker, and titrate the ferrous iron at once with standard potassium permanganate. Vanadium, carbonaceous material, soluble sulfides, and difficultly soluble minerals such as chromite, ilmenite, and magnetite, interfere to a greater or lesser extent.

VI. OXIDIZED LEAD

In this method all but the sulfide and chromate of lead are soluble.

To 1.0 gram of the material in a 250-ml. beaker, add 10 ml. of a saturated solution of ammonium acetate and 20 ml. of water. Boil for ten minutes and let stand hot for thirty minutes more. Filter, wash with hot water, and evaporate the filtrate to fumes with 5 to 10 ml. of sulfuric acid. Filter off the lead sulfate, and proceed as in the regular method.

VII. MnO_2 (AVAILABLE OXYGEN)

Place 0.5 gram of the finely ground ore in an 8-oz. flask. Add 25 ml. of water, 5 ml. of strong sulfuric acid, and as much of the usual standard oxalic acid solution delivered from a buret as may be judged necessary to decompose the MnO_2 present and leave a moderate excess of oxalic acid. More may be added later if found necessary. Boil gently until the decomposition of all MnO_2 is effected, adding more water or more oxalic acid solution as required. Finally, dilute, if necessary, with hot water, until the flask is about half full, and titrate with permanganate as usual. Multiply the percentage of manganese shown by 1.582 to obtain the percentage of MnO_2 .

VIII. OXIDE MOLYBDENUM

This method provides for the determination of oxidized molybdenum or molybdic ocher in molybdenite ores.

Place 5 grams of the ore in a 250-ml. beaker, add 50 ml. of 10 per cent hydrochloric acid, and stir in about 0.25 gram of paper pulp. Heat just to below boiling and maintain at this temperature for ten minutes. Filter on a close-textured 11-cm. filter paper, and wash well with hot 10 per cent hydrochloric acid. Determine molybdenum in the filtrate by the lead molybdate or α -benzoinoxime methods. Multiply the percentage of molybdenum by 1.500 to obtain the percentage of MoO_3 .

To obtain the percentage of molybdenite (MoS_2) deduct the oxide Mo from the total Mo and multiply by 1.668.

IX. FREE SULFUR IN ORES

Free sulphur is usually determined by extraction of the material with carbon bisulfide in a suitable extraction apparatus. This procedure does not extract amorphous sulfur, when present.

Have the material thoroughly air-dried. Heating to expel moisture is likely to volatilize sulfur. Weigh from 1 to 5 grams, according to amount of free sulfur possibly present. Place in a 200-ml. beaker, add about 30 ml. of aniline, and heat the mixture just to the boiling point for a few minutes, frequently rotating the beaker to stir the contents. Pour the hot liquid through a weighed Gooch crucible with asbestos mat, using suction. Rinse out the beaker several times with carbon disulfide, pouring through the residue in the crucible, until the crucible is washed free from aniline. A slight residue remaining in the beaker will soon dry and may be brushed into the crucible. Finally, heat the crucible to constant weight at about 100°C . The difference between the final weight of the residue and the original weight of substance taken represents the free sulfur.

It is best to have some water in the receiver under the Gooch filter, both to prevent the hot aniline from cracking the glass and to prevent the separated sulfur from adhering to the sides.

A possible source of error is water remaining in the substance that might count as free sulfur.

Caution should be used in handling the reagents as both aniline and carbon bisulfide are extremely poisonous.

X. OXIDE ZINC

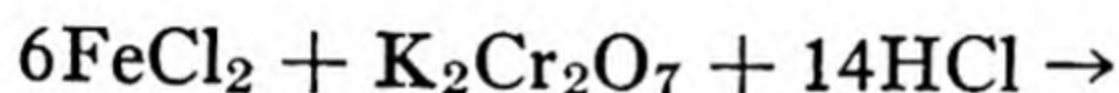
To 1.0 gram of the ore in a 250-ml. beaker, add 5 grams of ammonium chloride, 10 ml. of a saturated solution of ammonium acetate, and 25 ml. of water. Cover, boil for ten minutes, filter, and wash with a hot dilute ammonium chloride solution. Add 5 ml. of hydrochloric acid to the filtrate, and precipitate the ammonia group with ammonium hydroxide; add bromine water as in the regular procedure. Boil, filter, and determine the zinc in the filtrate as in the ferrocyanide method.

CHAPTER XXXIII

PREPARATION AND STANDARDIZATION OF SOLUTIONS

For technical work, when a great many determinations are performed each day, solutions are usually made up and standardized so that the number of milliliters used in the titration represents the percentage of the element present in the original material when 0.5 gram is taken for the analysis, or 1 ml. is equal to 0.005 gram of the element. The solutions are always made up slightly stronger than the theoretical strength and adjusted by dilution.

For example, a standard solution of potassium dichromate, such that 1 ml. is equal to 1 per cent of iron on a 0.5-gram basis, should contain 4.391 grams of the pure salt per liter of solution. This is shown by the equation:



Thus 1 molecule of potassium dichromate oxidizes 6 molecules of ferrous chloride to ferric chloride, or 1 molecule of $\text{K}_2\text{Cr}_2\text{O}_7 = 6\text{Fe}$. This corresponds to 294.22 parts of $\text{K}_2\text{Cr}_2\text{O}_7$ to 335.04 parts of Fe. Hence 1 per cent, or 0.005 gram of iron when 0.5 gram of ore is taken for assay, requires 0.004391 gram of $\text{K}_2\text{Cr}_2\text{O}_7$. If this amount is contained in 1 ml., then the liter will contain 4.391 grams of $\text{K}_2\text{Cr}_2\text{O}_7$.

In order to make the solution slightly stronger, 4.4 grams should be weighed out for each liter of solution. Then a stock of solution such as 20 liters will require 20 times 4.4 or 80.8 grams of $\text{K}_2\text{Cr}_2\text{O}_7$.

When the salt has completely dissolved, the solution is agitated and allowed to age for a day or two and then standardized against pure iron wire.

A weight of 0.2 gram of pure iron would be equivalent to a 0.5-gram portion of an ore containing 40 per cent of iron or should take exactly 40 ml. to titrate. If, for example, 39.4 ml. were used, then

20 liters minus 39.4 ml. leaves 19,960.6 ml. remaining

Then, $(19,960.6 \div 39.4)(40 - 39.4) = 304$, or the number of milliliters of water to be added.

Add about 290 ml. of water, mix, and allow the solution to age at least two weeks, when a final adjustment may be made in the same manner.

The use of a solution based on the normal system is sometimes an advantage. All such solutions correspond with one another, either directly or in a simple manner; each milliliter corresponds to an amount of the substance titrated that is at once deduced from its atomic or molecular weight.

Solutions that are used every day on a certain type of material are best standardized with standard samples of similar material.

The weights given for the following salts are the theoretical weights. The excess to be used in preparing a solution which may be adjusted by dilution should be judged by the analyst according to the age and purity of the reagent.

STANDARD NORMAL OR PERCENTAGE SOLUTIONS

1. Ammonium Molybdate

4.26 g. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ per liter.

1 cc. = 0.005 g. Pb.

Standardize as follows: Weigh carefully about 0.2 gram of pure lead foil and dissolve in a 150-ml. beaker by warming with a mixture of 2 ml. of strong nitric acid and 4 ml. of water. When dissolved, boil nearly or quite to dryness, add about 30 ml. of water, and see that all the lead nitrate dissolves. Now add 5 ml. of strong sulfuric acid, boil the mixture a moment, cool to room temperature, and allow to stand and settle a short time. Filter and wash with dilute (1 : 10) sulfuric acid. Proceed with the filtered lead sulfate precisely as described for the assay of an ore.

2. Ammonium or Potassium Thiocyanate

0.10 N.

7.612 g. NH_4CNS per liter, or

9.717 g. KCNS per liter.

1 ml. = 0.010030 g. Hg

= 0.016989 g. AgNO_3 .

0.10 *N*. 13.023 g. KCN per liter. 1 ml. = 0.002935 g. Ni.

Weigh up 13.5 grams of pure KCN and 5 grams of KOH, dissolve in water, and dilute to 1000 ml. Fill one buret with this solution and another with standard 0.10 *N* silver nitrate solution. Run 50 ml. of the cyanide solution into a large beaker, add 10 drops of a 5 per cent solution of potassium iodide and 10 ml. of ammonia, dilute to about 200 ml., and titrate with the silver nitrate solution until a distinct, but not too deep, yellowish cloud of silver iodide is formed, indicating that the end point has been reached. The cyanide will be found to be slightly stronger than the silver nitrate. For example: 51.3 ml. of the silver nitrate solution may have been required to neutralize 50 ml. of the cyanide solution, in which case add 1.3 ml. of water to each remaining 50 ml. of the cyanide. Another trial should demonstrate the two solutions to be of equal strength.

9. Potassium Dichromate

4.391 g. $K_2Cr_2O_7$ per liter. 1 ml. = 0.005000 g. Fe.

Dissolve 0.2 gram of pure iron wire in 20 to 40 ml. of 1 : 1 hydrochloric acid in a covered flask. Reduce the iron by the same method as used on the ore and titrate as given for the regular analysis.

10. Potassium Ferrocyanide

21.54 g. $K_4Fe(CN)_6 \cdot 3H_2O$ per liter. 1 ml. = 0.00500 g. Zn.

Dissolve 22.1 grams of $K_4Fe(CN)_6 \cdot 3H_2O$ and 0.3 gram $K_3Fe(CN)_6$ per liter of solution and standardize as follows: Weigh carefully about 0.2 gram of pure zinc into an 8-oz. flask and add 10 ml. of strong hydrochloric acid (sp. gr. 1.20). When the zinc has dissolved, dilute with about 25 ml. of water, add a few drops of litmus solution as an indicator, and make slightly alkaline with ammonia. Again acidify slightly with hydrochloric acid, and then add 3 ml. of the strong acid in excess. Dilute now to about 300 ml. with hot water and heat nearly to boiling. Titrate with the ferrocyanide solution in the regular manner.

10.19 g. $K_4Fe(CN)_6 \cdot 3H_2O$ per liter. 1 ml. = 0.0100 g. Pb.

Standardize by treating 0.3 to 0.4 gram of pure lead in the same manner as given for the analysis of an ore.

11. Potassium Iodate

29.455 g. KIO_3 per liter. 1 ml. = 0.005000 g. Cu.

If this salt is carefully dried at 105° C. and weighed to the exact figure given above, the solution will rarely need to be standardized and keeps indefinitely in a tightly stoppered bottle.

12. Potassium Permanganate

5.6359 g. KMnO_4 per liter.

1 ml. = 0.00500 g. CaO

0.00996 g. Fe

0.01086 g. Sb

0.00309 g. Cr (FeSO_4 reduction)

0.00490 g. Mn (H_2O_2 or oxalic acid method)

0.00294 g. Mn (Volhard method)

0.00196 g. Mn (bismuthate method)

0.00571 g. Mo (Zn reduction)

0.00908 g. V (HCl , SO_2 or FeSO_4 reduction)

0.01195 g. $\text{Na}_2\text{C}_2\text{O}_4$

0.01124 g. $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

0.10 N. 3.1606 g. KMnO_4 per liter.

1 ml. = 0.00509 g. V (HCl , SO_2 , FeSO_4 reduction)

0.00609 g. Sb

0.00280 g. CaO

0.00558 g. Fe

0.00173 g. Cr (FeSO_4 reduction)

0.01036 g. Pb

0.00320 g. Mo (Zn reduction)

0.00275 g. Mn (Julian or oxalic method)

0.00165 g. Mn (Volhard method)

0.00110 g. Mn (bismuthate method)

0.01191 g. U

0.00670 g. $\text{Na}_2\text{C}_2\text{O}_4$

0.00630 g. $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

2.8300 g. KMnO_4 per liter.

1 ml. = 0.00500 g. Fe

0.00545 g. Sb

0.00251 g. CaO

0.00155 g. Cr (FeSO_4 reduction)

0.00927 g. Pb

0.00287 g. Mo

0.00246 g. Mn (Julian or oxalic method)

0.00148 g. Mn (Volhard method)

0.00098 g. Mn (bismuthate method)

0.01066 g. U

0.00456 g. V (HCl , SO_2 , FeSO_4 reduction)

0.00600 g. $\text{Na}_2\text{C}_2\text{O}_4$

0.00564 g. $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Standardize the permanganate solutions with pure sodium oxalate as recommended by Fowler and Bright.¹ To 0.30 gram of pure sodium oxalate (dried at 105° C.) in a 400-ml. beaker, add 250 ml. of 5 per cent sulfuric acid previously heated to 25° to 30° C. Add 90 to 95 per cent of the permanganate solution required at a rate of 25 to 35 ml. per minute while stirring slowly. Allow time enough for the pink color to be discharged, heat to 55° to 60° C., and finish the titration, adding the last 0.5 ml. dropwise.

13. Silver Nitrate

0.20 *N.* 33.978 g. AgNO_3 or 21.576 g. Ag per liter.

1 ml. = 0.003800 g. F
0.015224 g. NH_4CNS
0.019435 g. KCNS
0.007092 g. Cl
0.026046 g. KCN
0.005869 g. Ni
0.028667 g. AgCl .

0.10 *N.* 16.989 g. AgNO_3 or 10.788 g. Ag per liter.

1 ml. = 0.002935 g. Ni
0.003546 g. Cl
0.007612 g. NH_4CNS
0.009717 g. KCNS
0.013023 g. KCN
0.002497 g. As
0.014334 g. AgCl .

1.626 g. AgNO_3 or 1.032 g. Ag per liter.

1 ml. = 0.002000 g. Bi
0.000728 g. NH_4CNS
0.000930 g. KCNS
0.001371 g. AgCl .

Standardize the pure dried silver nitrate crystals or pure silver dissolved in nitric acid by precipitating a measured amount of the solution with hydrochloric acid. Filter the well-coagulated precipitate of silver chloride in a tared Gooch crucible, wash with 1 per cent nitric acid, dry at 105° C., and weigh.

14. Sodium Hydroxide

0.10 *N.* 4.0005 g. per liter.

1 ml. = 0.002016 g. MgO
0.000135 g. P
0.003647 g. HCl

¹ R. M. Fowler and H. A. Bright, *Nat. Bur. Standards J. Research*, 15, 493, 1935.

0.006302 g. HNO_3
 0.004904 g. H_2SO_4
 0.020414 g. $\text{KHC}_8\text{H}_4\text{O}_4$
 0.012205 g. $\text{C}_7\text{H}_6\text{O}_2$.

Dissolve 5 grams of sodium hydroxide in about 300 ml. of distilled water. Add enough barium hydroxide to precipitate any carbonate present, filter into a liter flask, and dilute to volume with water that has been boiled and cooled to remove CO_2 . Standardize against pure potassium acid phthalate (0.5 gram dissolved in 100 ml. water), or benzoic acid (0.8 gram dissolved in 20 ml. alcohol), using phenolphthalein as indicator.

15. Sodium Thiosulfate

35.7905 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per liter.

1 ml. = 0.002500 g. Cr
 0.007072 g. $\text{K}_2\text{Cr}_2\text{O}_7$
 0.004558 g. KMnO_4 .

0.10 *N*. 24.8195 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per liter.

1 ml. = 0.000504 g. MgO (8-hydroxyquinoline method)
 0.004904 g. $\text{K}_2\text{Cr}_2\text{O}_7$
 0.003161 g. KMnO_4 .

19.5214 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per liter.

1 ml. = 0.005000 g. Cu
 0.005433 g. Pb
 0.003857 g. $\text{K}_2\text{Cr}_2\text{O}_7$
 0.002486 g. KMnO_4 .

Dissolve the weighed crystals in water, and add enough amyl alcohol to equal 1 per cent of the final volume. Standardize with a standard solution of permanganate as follows:

Place about 100 ml. of cold water in an 8-oz. flask. Add about 5 ml. of glacial acetic acid, and then run in from a buret about 35 ml. of the ordinary permanganate solution used for iron. Now add 6 ml. of 50 per cent potassium iodide solution and titrate with the thiosulfate solution while the permanganate buret is draining. When near the end, add a little starch solution and finish the titration carefully.

16. Sulfuric Acid

0.10 *N*. 4.904 g. H_2SO_4 per liter.

Take 3 ml. of pure concentrated H_2SO_4 (sp. gr. 1.84) per liter of solution, and standardize against 0.10 *N* sodium hydroxide, using phenolphthalein as indicator. One milliliter = 0.004 g. NaOH .

INDICATOR SOLUTIONS

1. Brom phenol Blue

Dissolve 0.4 gram of the powdered reagent in 6 ml. of 0.10 *N* sodium hydroxide, and dilute to 100 ml.

2. Ferric Ammonium Sulfate

Make a cold saturated water solution of the ferric alum, and add enough nitric acid to bleach the brown color.

3. Methyl Orange

A 0.1 per cent solution in distilled water.

4. Methyl Red

A 0.2 per cent alcoholic solution.

5. Phenolphthalein

Dissolve 1 gram in 50 ml. of alcohol, and dilute with water to 100 ml.

6. Potassium Chromate

A 2 per cent aqueous solution.

7. Potassium Ferricyanide

A 0.7 per cent aqueous solution prepared fresh each time it is used.

8. Starch

Dissolve 1 gram of soluble starch in 200 ml. of boiling distilled water, and add 0.5 gram of salicylic acid. Cool before using.

9. Tannic Acid

Dissolve 1 gram of tannic acid in 300 ml. of water, and add a few drops of a saturated solution of mercury bichloride. A little blue dye added to this solution tends to overcome the yellow color of the tannic acid and gives a clearer drop.

10. Uranium Acetate

A saturated aqueous solution.

SPECIAL REAGENTS

1. Molybdic Acid Reagent for Phosphorus

Mix 100 grams of molybdic acid to a paste, with 265 ml. of water. Add 155 ml. of strong ammonia water (sp. gr. 0.90), and stir until all is dissolved. To this solution add 66 ml. of strong nitric acid (sp. gr. 1.42), stir well, and then set aside for an hour. In another vessel make a mixture of 395 ml. of strong nitric acid and 1100 ml. of water. Finally, pour the first solution into the second, stirring constantly. Allow to stand for twenty-four hours before using.

2. Magnesia Mixture

Dissolve 400 grams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 300 grams of NH_4Cl in 1500 ml. of warm water. Add ammonium hydroxide until alkaline, and allow to stand for an hour. Filter, and add hydrochloric acid to the filtrate until acid to litmus paper.

3. Standard Chromium Solution

Dissolve 0.2828 gram of pure recrystallized potassium dichromate in distilled water, and dilute to exactly 1 liter. One milliliter of this solution contains 0.0001 gram of chromium.

4. Standard Iron Solution

Dissolve 0.1000 gram of pure iron wire in 10 ml. of iron-free hydrochloric acid. Add 5 ml. of 1 : 1 perchloric acid, and dilute to exactly 1 liter. One milliliter contains 0.0001 gram of iron.

5. Standard Manganese Solution

Dissolve 0.2877 gram of pure potassium permanganate in distilled water, and dilute to exactly 1 liter. One milliliter will contain 0.0001 gram of manganese.

6. Standard Titanium Solution

Fuse 0.1000 gram of pure titanium dioxide, in a silica crucible, with 5 grams of potassium pyrosulfate. The crucible should be covered during the fusion and care taken that none of the melt is lost through spattering. Dissolve the melt in 10 per cent sulfuric acid, and carefully wash the crucible and cover with the same strength of acid solution. Dilute to exactly 1 liter with 10 per cent sulfuric acid. One milliliter will contain 0.0001 gram of TiO_2 .

TABLES

TABLE OF MEASURES AND WEIGHTS

MEASURES OF CAPACITY

A. DRY MEASURE

1 bushel = 2150.42 cubic inches.

1 bushel = the volume of 77.627 pounds of distilled water at 4° C.

Legal: 1 liter = 0.908 quart.

1 bushel = 4 pecks = 8 gallons = 32 quarts = 35.24229 liters.

1 peck = 2 gallons = 8 quarts = 8.81057 liters.

1 gallon = 4 quarts = 4.40528 liters.

1 quart = 1.10132 liters.

B. LIQUID MEASURE

1 U. S. gallon = 231 cubic inches.

1 gallon = the volume of 8.3388822 pounds = 58378 troy grains of distilled water at 4° C. (Stillman, Engineering Chemistry.)

1 gallon = 58318 grains of water at 62° F. (U. S. Phar.)

1 gallon = 58334.9 + grains of pure water at 60° F., weighed in air at 60° F., at barometric pressure of 30 inches of mercury. (Mason, Examination of Water.)

Legal: 1 liter = 1.0567 quart = 0.26417 gallon.

1 gallon = 4 quarts = 8 pints = 32 gills = 3.78544 liters.

1 quart = 2 pints = 8 gills = 0.94636 liter.

1 pint = 4 gills = 0.47318 liter.

1 gill = 0.118295 liter.

1 cubic foot = 7.48 gallons = 28.315 liters = 62.42 pounds of water at 60° F. (Stillman.)

1 cubic foot of water at 62° F. = 62.355 pounds avoirdupois = 28,320 grams.

1 cubic inch of water at 62° F. = 0.0361 pound avoirdupois = 16.387 grams. (Watts' Dictionary, V, 1010.)

LINEAR MEASURE

1 yard = 0.91440 meter.

1 foot = 0.30480 meter.

1 inch = 0.0254 meter.

39.37 inches = 1 meter.

WEIGHTS

1 grain troy = 0.0648004 gram.

1 pound troy = 0.822857 pound avoirdupois.

1 pound avoirdupois = 7000 grains troy = 1.215279 pounds troy.

TROY WEIGHT

1 pound	=	12 oz.	=	240 pennyweights	=	5760 grains	=	373.2418 grams.
		1 oz.	=	20 pennyweights	=	480 grains	=	31.1035 grams.
				1 pennyweight	=	24 grains	=	1.5552 grams.
						1 grain	=	0.0648 gram.
				1 gram	=	15.432 troy grains.		

AVOIRDUPOIS WEIGHT

1 ton	=	20 hundredweight	=	2240 pounds	=	1016.04 kilograms.
		1 hundredweight	=	112 pounds	=	50.80 kilograms.
1 pound	=	16 ounces	=	256 drams	=	7000.00 grains = 453.5900 grams.
		1 ounce	=	16 drams	=	437.50 grains = 28.3495 grams.
				1 dram	=	27.34 grains = 1.7718 grams.
1 net ton	=	2000 pounds	=	29,166 $\frac{2}{3}$ ounces troy	=	907.19 kilograms.

METRIC TON

1 metric ton = 1000 kilograms.

CONVERSION OF THERMOMETER READINGS

To convert Fahrenheit to Centigrade, subtract 32 and multiply by $\frac{5}{9}$.
To convert Centigrade to Fahrenheit, multiply by $\frac{9}{5}$ and add 32.

BEAKER NUMBERS AND CORRESPONDING CAPACITIES

Number.	Capacity, ml.	Number.	Capacity, ml.
000	15	5	500
00	35	6	700
0	55	7	900
1	100	8	1500
2	150	9	2000
3	250	10	2600
4	350		

PERCENTAGE SOLUTIONS

In this book the percentage of a salt in a solution is taken as the weight in grams in 100 ml. of the solution. This, of course, does not express the actual percentage correctly, but the system is easily understood and is used for convenience. Thus, a 10 per cent solution of a salt means 10 grams dissolved in the liquid and made up to 100 ml.

CHEMICAL FACTORS

Determined	Sought	Factor
Aluminum		
Al_2O_3	Al	0.5291
	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (diaspore)	1.1767
	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (bauxite)	1.3535
	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (gibbsite)	1.5302
	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (andalusite)	1.4028
	Na_3AlF_6 (cryolite)	4.1193
AlPO_4	Al_2O_3	0.4178
$\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$	Al	0.0587
	Al_2O_3	0.1110
Antimony		
Sb	Sb_2S_3 (stibnite)	1.3950
	Sb_2O_3 (senarmontite)	1.1971
	Sb_4O_8 (cervantite)	1.2628
Arsenic		
As	As_2O_3	1.3204
	As_2S_3	1.6420
	FeAsS (arsenopyrite)	2.1734
	$3\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_5$ (enargite)	5.2578
As_2S_3	As	0.6090
	As_2O_3	0.8041
$\text{Mg}_2\text{As}_2\text{O}_7$	As	0.4826
	As_2O_3	0.6372
Barium		
BaSO_4	Ba	0.5885
	BaO	0.6570
	BaCO_3 (witherite)	0.8455
BaCrO_4	Ba	0.5421
	BaO	0.6053
	BaCO_3	0.7789
	BaSO_4	0.9212
Beryllium		
BeO	$3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (beryl)	7.1590
	$\text{BeO} \cdot \text{Al}_2\text{O}_3$ (chrysoberyl)	5.0743
	$2\text{BeO} \cdot \text{SiO}_2$ (phenacite)	2.2002
	Be	0.3605
Bismuth		
BiOCl	Bi	0.8024
	Bi_2O_3	0.8946

CHEMICAL FACTORS—*Continued*

Determined	Sought	Factor
Bismuth—Continued		
	Bi_2S_3 (bismuthinite)	0.9871
Bi_2O_3	Bi	0.8970
	Bi_2S_2	1.1034
Cadmium		
Cd	CdS (greenockite)	1.2852
CdSO_4	Cd	0.5392
	CdS	0.6930
Calcium		
CaO	CaCO_3 (calcite)	1.7846
	CaF_2 (fluorite)	1.3923
	CaSO_4 (anhydrite)	2.4276
	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum)	3.0701
	Ca	0.7147
CaCO_3	Ca	0.4005
	CaO	0.5603
	CO_2	0.4396
CaSO_4	Ca	0.2944
	CaO	0.4119
	SO_3	0.5881
Carbon		
CO_2	BaCO_3 (witherite)	4.4855
	CaCO_3 (calcite)	2.2745
	FeCO_3 (siderite)	2.6327
	MgCO_3 (magnesite)	1.9164
	MnCO_3 (rhodochrosite)	2.6120
	PbCO_3 (cerussite)	6.0732
	SrCO_3 (strontianite)	3.3552
	ZnCO_3 (smithsonite)	2.8491
BaCO_3	CO_2	0.2229
Chlorine		
Cl	HCl	1.0284
	AgCl (cerargyrite)	4.0426
	KCl (sylvite)	2.1027
	NaCl (halite)	1.6486
AgCl	Cl	0.2474
	HCl	0.2544

CHEMICAL FACTORS—*Continued*

Determined	Sought	Factor
Chromium		
Cr	Cr ₂ O ₃	1.4614
	FeO·Cr ₂ O ₃ (chromite)	2.1521
	PbCrO ₄ (crocoite)	6.2148
Cr ₂ O ₃	Cr	0.6842
	FeO·Cr ₂ O ₃	1.4726
	PbCrO ₄	4.2525
K ₂ Cr ₂ O ₇	Cr	0.3536
	Cr ₂ O ₃	0.5167
Cobalt		
Co	CoO	1.2715
	Co ₃ O ₄	1.3620
Co ₃ O ₄	Co	0.7342
	CoO	0.9336
Copper		
Cu	CuO (tenorite)	1.2517
	Cu ₂ O (cuprite)	1.1258
	CuS (covellite)	1.5043
	Cu ₂ S (chalcocite)	1.2522
	CuFeS ₂ (chalcopyrite)	2.8871
CuO	Cu	0.7989
Cu ₂ O	Cu	0.8882
CuS	Cu	0.6647
Cu ₂ S	Cu	0.7986
Fluorine		
CaF ₂	F	0.4867
F	CaF ₂ (fluorite)	2.0547
	Na ₃ AlF ₆ (cryolite)	1.8418
PbClF	F	0.0726
Iron		
Fe	FeO	1.2865
	Fe ₂ O ₃ (hematite)	1.4298
	Fe ₃ O ₄ (magnetite)	1.3820
	FeO·Cr ₂ O ₃ (chromite)	4.0090
	FeO·TiO ₂ (ilmenite)	2.7174
	FeCO ₃ (siderite)	2.0747

CHEMICAL FACTORS—*Continued*

Determined	Sought	Factor
Iron—Continued		
	FeS ₂ (pyrite).....	2.1483
	FeAsS (arsenopyrite).....	2.9157
	CuFeS ₂ (chalcopyrite).....	3.2867
Fe ₂ O ₃	Fe.....	0.6994
	FeO.....	0.8998
Lead		
Pb.....	PbO.....	1.0772
	PbCO ₃ (cerussite).....	1.2895
	PbSO ₄ (anglesite).....	1.4636
	PbS (galena).....	1.1547
	PbMoO ₄ (wulfenite).....	1.7719
	PbCrO ₄ (crocoite).....	1.5598
PbS.....	Pb.....	0.8660
	PbO.....	0.9329
PbSO ₄	Pb.....	0.6833
	PbO.....	0.7360
Magnesium		
Mg ₂ P ₂ O ₇	Mg.....	0.2184
	MgO.....	0.3621
	MgCO ₃ (magnesite).....	0.7573
	Mg(OH) ₂ (brucite).....	0.5239
	MgSO ₄	1.0812
	MgSO ₄ ·7H ₂ O.....	2.2138
MgO.....	Mg.....	0.6032
Mg(C ₉ H ₆ ON) ₂	Mg.....	0.0778
	MgO.....	0.1290
Manganese		
Mn.....	MnO ₂ (pyrolusite).....	1.5825
	MnCO ₃ (rhodochrosite).....	2.0923
	MnO.....	1.2913
	Mn ₂ O ₃	1.4369
	Mn ₃ O ₄	1.3884
MnO ₂	Mn.....	0.6319
	Mn ₂ O ₃	0.9080
KMnO ₄	Mn.....	0.3476
	MnO ₂	0.5501
	Mn ₂ O ₃	0.4995

CHEMICAL FACTORS—*Continued*

Determined	Sought	Factor
Mercury		
Hg.....	HgO.....	1.0798
	HgS (cinnabar).....	1.1598
Molybdenum		
Mo.....	MoO ₃	1.5003
	MoS ₂ (molybdenite).....	1.6683
	PbMoO ₄ (wulfenite).....	3.8266
MoO ₃	Mo.....	0.6665
	MoS ₂	1.1120
	PbMoO ₄	2.5506
PbMoO ₄	Mo.....	0.2613
	MoO ₃	0.3921
	MoS ₂	0.4360
Nickel		
Ni.....	NiO.....	1.2726
	NiS (millerite).....	1.5463
	NiAs (niccolite).....	2.2764
	2FeS·NiS (pentlandite).....	4.5416
Ni(C ₄ H ₇ N ₂ O ₂) ₂	Ni.....	0.2032
	NiO.....	0.2586
	NiS.....	0.3141
	NiAs.....	0.4624
	2FeS·NiS.....	0.9226
Phosphorus		
Mg ₂ P ₂ O ₇	P.....	0.2786
	PO ₄	0.8534
	P ₂ O ₅	0.6379
(NH ₄) ₃ PO ₄ ·12MoO ₃ ...	P.....	0.0165
	PO ₄	0.0506
	P ₂ O ₅	0.0378
Potassium		
KCl.....	K.....	0.5244
	K ₂ O.....	0.6317
	K ₂ CO ₃	0.9268
K ₂ O.....	K.....	0.8301
	KCl (sylvite).....	1.5835
	K ₂ CO ₃	1.4671
	K ₂ SO ₄	1.8499
K ₂ PtCl ₆	K.....	0.1608

CHEMICAL FACTORS—*Continued*

Determined	Sought	Factor
Potassium—<i>Continued</i>		
	KCl.....	0.3607
	K ₂ O.....	0.1938
	K ₂ CO ₃	0.2843
	K ₂ SO ₄	0.3584
Silicon		
SiO ₂	Si.....	0.4672
Silver		
AgCl.....	Ag.....	0.7526
	Cl.....	0.2474
Ag.....	AgCl.....	1.3287
	Cl.....	0.3287
Sodium		
NaCl.....	Na.....	0.3934
	Cl.....	0.6066
	AgCl.....	2.4521
	Na ₂ O.....	0.5303
	NaNO ₃ (soda niter).....	1.4542
	Na ₂ SO ₄ (thenardite).....	1.2151
	Na ₂ CO ₃	0.9066
Na ₂ O.....	Na.....	0.7419
	NaCl (halite).....	1.8858
	NaNO ₃	2.7424
	Na ₂ SO ₄	2.2914
	Na ₂ CO ₃	1.7097
Strontium		
SrO.....	Sr.....	0.8456
	SrCO ₃ (strontianite).....	1.4246
	SrSO ₄	1.7726
SrSO ₄	Sr.....	0.4771
	SrO.....	0.5642
	SrCO ₃	0.8037
Sulfur		
BaSO ₄	S.....	0.1374
	SO ₂	0.2744
	SO ₃	0.3430
	H ₂ SO ₄	0.4202
	FeS ₂ (pyrite).....	0.2570

CHEMICAL FACTORS—Continued

Determined	Sought	Factor
Sulfur—Continued		
S	Sb ₂ S ₃ (stibnite)	3.5319
	Bi ₂ S ₃ (bismuthinite)	5.3460
	CdS (greenockite)	4.5062
	CuS (covellite)	2.9828
	Cu ₂ S (chalcocite)	4.9657
	FeS ₂ (pyrite)	1.8709
	FeAsS (arsenopyrite)	5.0783
	PbS (galena)	7.4632
	HgS (cinnabar)	7.2573
	MoS ₂ (molybdenite)	2.4964
	NiS (millerite)	2.8306
	ZnS (sphalerite)	3.0393
SO ₃	BaSO ₄ (barite)	2.9156
	CaSO ₄ (anhydrite)	1.7005
	CaSO ₄ · 2H ₂ O (gypsum)	2.1505
	PbSO ₄ (anglesite)	3.7880
	MgSO ₄	1.5036
	K ₂ SO ₄	2.1766
	Na ₂ SO ₄ (thenardite)	1.7743
Tin		
Sn	SnO ₂	1.2696
Titanium		
Ti	TiO ₂ (rutile)	1.6681
	FeO · TiO ₂ (ilmenite)	3.1678
TiO ₂	Ti	0.5995
Tungsten		
W	WO ₃	1.2609
WO ₃	W	0.7931
Uranium		
U	U ₃ O ₈	1.1792
U ₃ O ₈	U	0.8481
(UO ₂) ₂ P ₂ O ₇	U	0.6668
	U ₃ O ₈	0.7862

CHEMICAL FACTORS—Continued

Determined	Sought	Factor
Vanadium		
V.....	V ₂ O ₅	1.7851
V ₂ O ₅	V.....	0.5602
Zinc		
Zn.....	ZnO (zincite).....	1.2447
	ZnS (sphalerite).....	1.4904
	ZnCO ₃ (smithsonite).....	1.9179
ZnO	Zn.....	0.8034
	ZnS.....	1.1973
	ZnCO ₃	1.5407
Zn ₂ P ₂ O ₇	Zn.....	0.4290
	ZnO.....	0.5340
ZnS	Zn.....	0.6710
	ZnO.....	0.8352
Zirconium		
Zr.....	ZrO ₂	1.3508
ZrO ₂	Zr.....	0.7403
Zr ₂ P ₂ O ₇	Zr.....	0.5118
	ZrO ₂	0.6913

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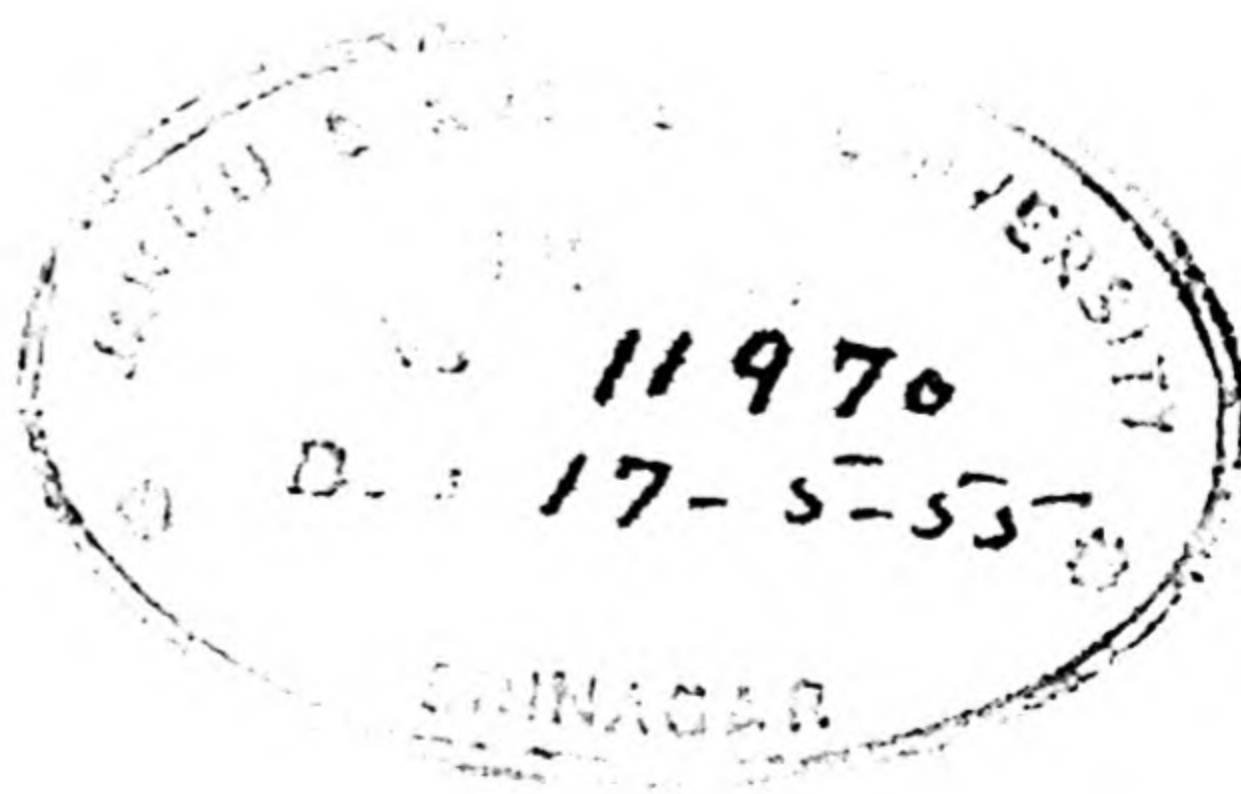
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